product was eluted with dilute ammonium hydroxide and concentrated to dryness. The compounds were dried azeotropically with ethanol.

(−)-9-(*trans*-2′,*trans*-3′-Dihydroxycyclopent-4′-enyl)-adenine (14): yield 230 mg (98%); mp 175–176 °C; $[\alpha]_D$ −170° (*c* 1.0, H_2O); ^1H NMR ($DMSO$-d_6 + D_2O) δ 8.47 (s, 2 H, H-2, H-8), 6.09 (m, 2 H, H-4′ and H-5′), 5.45 (d, 1 H, H-1′, *J* = 6 Hz), 4.55 (d, 1 H, H-3′, *J* = 6 Hz), 4.25 (dd, 1 H, H-2′, *J* = 6 Hz); MS (QP-El-Probe), *m/e* 233 (M^+ 1), 216 (− HO), 135 (base, adenine). Anal. ($C_{10}H_{11}N_5O_2{\cdot}H_2O$) C, H, N.

(−)-9-(*trans*-2′,*trans*-3′-Dihydroxycyclopent-4′-enyl)-3-deazaadenine (15): yield 305 mg (98%); mp 140 °C; $[\alpha]_D$ −210° (*c* 1.1, MeOH); UV_{max} 263 nm, 267 nm (sh). ^1H NMR ($DMSO$-d_6 + D_2O) δ 8.03 (s, 1 H, H-2), 7.64 (d, 1 H, H-6, *J* = 6 Hz), 6.76 (d, 1 H, H-7, *J* = 6 Hz), 6.13 (m, 2 H, H-4′ and H-5′), 5.29 (d, 1 H, H-1′, *J* = 5 Hz), 4.49 (d, 1 H, H-3′, *J* = 5 Hz), 4.05 (dd, 1 H, H-2′, *J* = 5 Hz); MS (D-El, MeOH), *m/e* 232 (M^+) peak match Δ = 0.0007, 215 (− HO), 134 (base, 3-deazaadenine). Anal. ($C_{11}H_{12}N_4O_2{\cdot}EtOH$) C, H, N.

Acknowledgment. This work was supported by the U. S. Public Health Services (Grant GM-29332).

Generation and Nuclear Magnetic Resonance Studies of 9-Heteroanthracenide Anions: 9-Selena-, 9-Phospha-, and 9-Arsaanthracenides

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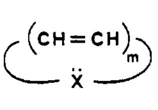
The thermally stable heteroanthracenide ions **9d–g** were generated upon exposure of the respective conjugate acids **8d–g** to KNH_2 in liquid NH_3 and were studied by ^1H, ^{13}C, and ^{31}P NMR. It is shown that **9d** possesses a paratropic molecular frame, while **9e** and **9f** exhibit no detectable paramagnetic ring current effect. Possible electronic and steric interactions that may give rise to the observed NMR characteristics of **9e–g** are discussed, and it is concluded that the carbanionic charge in these anions is substantially delocalized over the central ring involving the heteroatomic unit.

The influence of heteroatoms on the development of potential aromaticity (in "4*n* + 2" electron π-excessive[2] system **1**, *m* = even integer) and antiaromaticity (in "4*n*" electron counterpart **1**, *m* = odd integer) has been the subject of extensive theoretical[3] and experimental[4] work. Of considerable interest in this area is the direct observation and possible characterization of potentially delocalizable bis-π-excessive systems such as **2**, which incorporates a second π-excessive unit, namely, a carbanionic center in addition to a heteroatomic unit.



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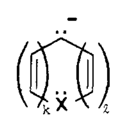

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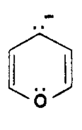
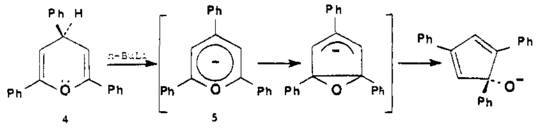


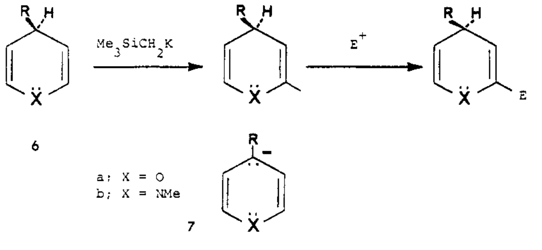
3

Research aimed at the generation and direct observation of the potentially antiaromatic 8 π-electron anions **2** (*k* = *l* = 1) was pioneered by Schmidt and co-workers.[5] All attempts at observing **3** were unsuccessful, and in the case of substituted anion **5** were frustrated by its rapid ring-contractive reorganization to yield the cyclopentadiene derivative shown in eq 1.



(1)

In a related study,[6] metalation of **6** by the powerful metalating agent [(trimethylsilyl)methyl]potassium resulted in a slow hydrogen/potassium exchange at the α-position to the heteroatom rather than at the activated double allylic γ-position (eq 2), indicating the relative instability of the incipient eight π-electron anions **7a** and **7b**.



(2)

Our work in this area included a study (by NMR) of certain dibenzannulated variants of **2**, namely, anions **9a**[7] (4*n* π-electrons) and **11**[8] (4*n* + 2 π-electrons), which were

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(1) Present address: Chemistry Department, East Tennessee State University, Johnson City, TN 37614.

(2) A π-excessive system is defined as a π-conjugated system containing more π-electrons than the ring atoms: Albert, A. *Heterocyclic Chemistry: An Introduction*; Athlone: London, 1968.

(3) (a) Hückel, E. *Z. Phys.* **1931**, *70*, 204. (b) Hückel, E. *Ibid.* **1932**, *76*, 628. (c) Dewar, M. J. S.; Harget, A. J.; Trinajstic', N.; Worley, S. D. *Tetrahedron* **1970**, *26*, 4504. (d) Hess, B. A., Jr.; Schaad, L. J.; Holyoke, C. W., Jr. *Ibid.* **1972**, *28*, 3657. (e) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1973**, *95*, 3907.

(4) For reviews, see: (a) Cook, M. J.; Katritzky, A. R.; Lunda, P. In *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Boulton, A. J., Eds.; Academic: New York, 1974; Vol. 17, p 255. (b) Anastassiou, A. G. *Acc. Chem. Res.* **1972**, *5*, 281. (c) Anastassiou, A. G. In *Topics in Nonbenzenoid Aromatic Chemistry*; Nozoe, T., Breslow, R., Hafner, K., Ito, S., Murata, I., Eds.; Hirokawa: Tokyo, 1973; Vol. 1, p 1. (d) Anastassiou, A. G. *Acc. Chem. Res.* **1976**, *9*, 453. (e) Anastassiou, A. G.; Kasmai, H. S. *Adv. Heterocycl. Chem.* **1978**, *23*, 55.

(5) Schmidt, R. R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 581.

(6) Schlosser, M.; Schneider, P. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 489.

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(8) Anastassiou, A. G.; Kasmai, H. S. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 393.

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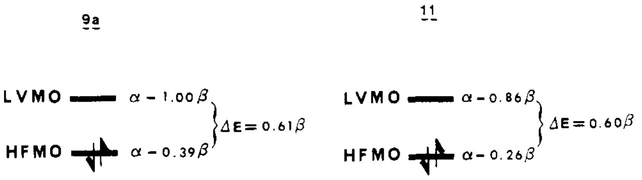
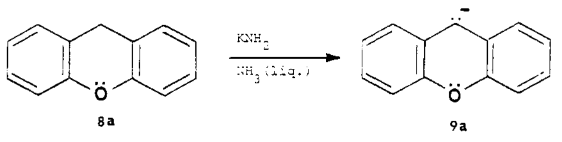
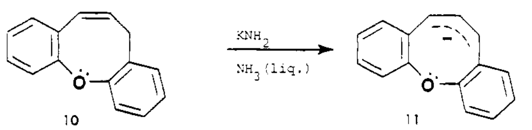


Figure 1. HMO frontier orbital energies for **9a** and **11**. HMO parameters[3d] employed: $h_{C^-} = -1.0$, $h_{\ddot{O}} = +2.0$, and $k_{CO} = 0.34$.

generated by treating the respective hydrocarbon acids **8a** and **10** with KNH_2 in liquid NH_3 (eq 3 and 4).



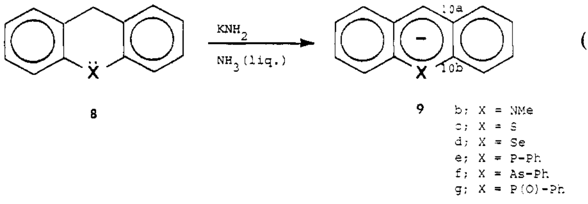
(3)



(4)

The result of these studies indicated that while anion **9a** is a thermally stable[9] and paratropic[10] 4n π-electron species, the 4n + 2 π-electron anion **11** does not realize its potential aromatic delocalization and may be best regarded as a molecule in which the negative charge is primarily localized in the allylic moiety of the eight-membered ring. This contrast, interestingly, arises from the controlling influence of skeletal factors (which impose a flat frame on the central ring of **9a** and a heavily buckled one on that of **11**) and electronic effects. Within the limits of simple Hückel molecular orbital theory, our calculations (shown partially in Figure 1) indicate the presence of a fully occupied and slightly antibonding HFMO and a HFMO/LVMO energy gap[11] of ca. 0.60β for both **9a** and **11**.

In order to examine the influence of the heteroatom on the exact location of HFMO, on the HFMO/LVMO energy gap, and on the development of paratropicity in the 4n π-electron heteroanthracenide anion, the nitrogen and sulfur analogues of **9a** (namely **9b** and **9c**, eq 5) were studied[12] next. It was found that (a) anion **9b**, a thermally stable species, is endowed with a molecular paratropicity similar to oxygen analogue **9a** and (b) anion **9c** exhibits NMR characteristics that are fundamentally different from those of **9a** and **9b**. Specifically, whereas **9c** is clearly less paratropic than either **9a** or **9b**, the key carbanionic proton (H-10) and carbon (C-10) chemical shifts in the NMR of **9c** are strongly indicative of the fact that the negative charge in **9c** is the least localized of the three. This operational inconsistency between the heteroatom's effectiveness with regard to the extent of carbanionic charge delocalization (O < NMe < S) and the development of paratropicity (S < O ~ NMe) was attributed to the sulfur atom's ability as a second-row element to stabilize an adjacent negative charge, thereby leading to a diminished overall delocalization of the charge.



(5)

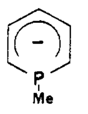
Table I. ^1H and ^{13}C NMR Data for 9d-f[a]

	^1H NMR		^{13}C NMR	
anion	"benzenoid"	H-10	C-10 (J_{CH})	"quaternary"
9d	5.59–6.21	3.97	84.23 (149.7)	110.01, 148.23
9e	6.19–7.34	5.08	89.24 (149.2)	111.23, 145.72, 149.20
9f	6.04–7.24	4.86	88.25 (149.0)	116.60, 143.7, 145.35

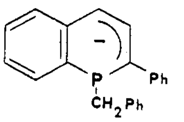
[a] All spectra recorded in liquid ammonia at ca. 24 °C. Chemical shifts (δ values) are given relative to TMS and were measured from the central signal of the low-field multiplet of THF-d_8 (δ 3.7 for proton and δ 67.9 for carbon). Coupling constants are in hertz.

The question of the nature of bonding available to anion **9c** and the possibility of "π-electron donation" to the vacant d orbital of the heteroatom[13] urged us to examine the effect of other second-row (phosphorus) and third-row (arsenic and selenium) heteroatoms on the development of paratropicity and/or delocalization of the carbanionic charge in the anthracenide system.

The choice of phosphorus and arsenic were of particular interest since it has been found that the alkyl-substituted heterocarbanions **12**[14a] and **13**[14b] undergo alkylation at the 2- and 4-positions, while the phenyl-substituted anion **14**[14c] was alkylated at the phosphorus. In the case of **12**, the results of ^1H and ^{13}C NMR studies led Ashe et al.[14a] to the conclusion that there is no strong electronic interaction between the heteroatom and the carbanionic pentadienyl system in **12**.



12 ; X = P, As, Sb



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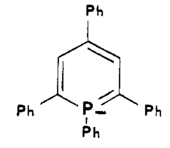

14

In this paper, we describe our work on the generation (eq 5) and ^1H, ^{13}C, and ^{31}P NMR studies of heteroanthracenide anions **9** incorporating selenium (**9d**), phosphorus (**9e** and **9g**), and arsenic (**9f**).

Results and Discussion

Syntheses. The conjugate acid progenitors **8d**[15] and **8f**[16] were prepared according to the published literature. A synthesis of **8e** reported by Bickelhaupt et al.[17] involves

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[9] The ^1H NMR spectrum of the anion shows no qualitative or quantitative deterioration upon hours of exposure to ambient temperature and shows very little deterioration after storage in a freezer for a period of over 1 year.

[10] Paratropic systems exhibit a paramagnetic ring current shielding in the ^1H NMR spectrum.

[11] The magnitude of the paratropic ^1H NMR chemical shifts in 4n-electron-charged hydrocarbon systems has been found to depend linearly upon the magnitude of HFMO/LVMO energy gaps: Minsky, A.; Meyer, A. Y.; Robinovitz, M. *Tetrahedron* **1985**, *41*, 785.

[12] Anastassiou, A. G.; Kasmai, H. S.; Saadein, M. R. *Tetrahedron Lett.* **1980**, 3743.

[13] For a discussion of d_π–P_π bonding, see: (a) Dewar, M. J. S. *The Molecular Orbital Theory of Organic Chemistry*; McGraw-Hill: New York, 1969; p 430. (b) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.

[14] (a) Ashe, A. J.; Smith, T. W. *Tetrahedron Lett.* **1977**, 407. (b) Maerkl, G.; Heier, K. H. *Ibid.* **1974**, 4501. (c) Maerkl, G.; Merz, A. *Ibid.* **1971**, 1215.

[15] (a) Sindelar, K.; Svatek, E.; Metysova, J.; Metys, J.; Protiva, M. *Collect. Czech. Chem. Commun.* **1969**, *34*, 3792. (b) Urberg, M. M.; Kaiser, E. T. *J. Am. Chem. Soc.* **1967**, *89*, 5931.

[16] (a) Bickelhaupt, R.; Jongsma, C.; de Koe, P.; Lourens, R.; Mast, N. R.; van Mourik, G. L.; Vermeer, H.; Weustink, R. J. M. *Tetrahedron* **1976**, *32*, 1921. (b) Bergmann, E. *J. Org. Chem.* **1939**, *4*, 1. (c) Issleib, K.; Seidel, W. *Chem. Ber.* **1959**, *92*, 2681. (d) de Koe, P. Doctoral Dissertation, Vrije University, Amsterdam, The Netherlands, 1969. A copy was provided by Professor Bickelhaupt. (e) Gump, W.; Stoltzenberg, H. *J. Am. Chem. Soc.* **1931**, *53*, 1428. (f) Jones, E. R. H.; Mann, F. G. *J. Chem. Soc.* **1958**, 294.

[17] Jongsma, C.; Lourens, R.; Bickelhaupt, F. *Tetrahedron* **1976**, *32*, 121.

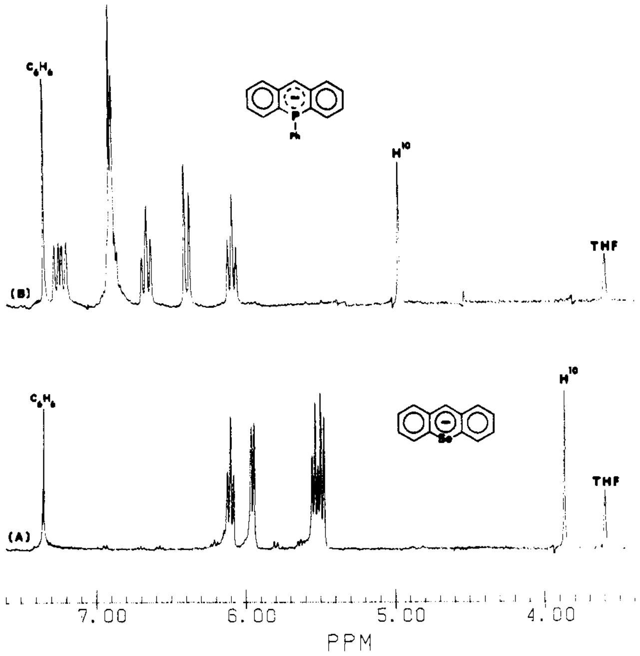
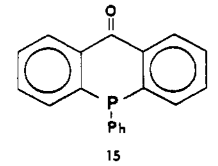


Figure 2. ^{1}H NMR spectrum of (A) 9,10-dihydro-9-selenaanthracenide anion (**9d**) recorded at 360 MHz and (B) 9,10-dihydro-9-phenyl-9-phosphaanthracenide anion (**9e**) recorded at 250 MHz (plotted on the same scale) in liquid ammonia (THF and C_6H_6, <1%, as internal standards) at ca. 24 °C.

a nine-step reaction sequence starting with 2-bromobenzaldehyde with an overall yield of ca. 3%. We have prepared **8b** from **15** by a modified aluminum hydride reduction.[18] The intermediate **15** was prepared from 2-bromotoluene as described by Granoth et al.[19] The overall yield of **8e** was 19%. Phosphine oxide **8g**[17] was obtained from the oxidation of **8e** with 30% hydrogen peroxide (eq 6).



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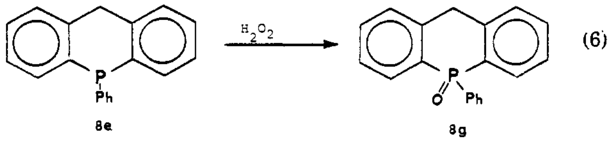

(6)

8e 8g

Generation and NMR Measurements of Heteroanthracenide Anions 9d–g. Treatment of **8d–f** with potassium amide in liquid ammonia at −78 °C, followed by warming to 0 °C, resulted in quantitative yields of thermally stable[9] and intensely colored anions **9d–f**,[20] respectively. The key NMR characteristics of these anions are shown in Table I and Figure 2.

Table II. ^{1}H and ^{13}C NMR Data for 8c–f and 9c–f[a]

conjugate acid → anion	H-10	C-10
8c → **9c**	3.86 → 3.92	39.00 → 82.67
8d → **9d**	3.95 → 3.97	43.70 → 84.23
8e → **9e**	3.96[b] → 5.08	40.71 → 89.24
8f → **9f**	3.94 → 4.86	42.51 → 88.25

[a] All spectra recorded in liquid ammonia at ca. 24 °C. Chemical shifts (δ values) are given relative to TMS and were measured from the central signal of the low-field multiplet of THF-d_8 (δ 3.7 for proton and δ 67.9 for carbon). [b] The average of the observed chemical shifts for two benzylic protons.

The recorded NMR data clearly show the following: (a) The formally "benzenoid" protons of **9d** experience a moderate shielding effect (δ 1.56 shift for the center of absorption manifold) on passing from the conjugate acid **8d** to the anion **9d**. This shift, which is slightly larger than that observed for the sulfur anion **9c**[12] (δ 1.3 for the center of benzenoid absorption manifold), implicates the presence of a paratropic molecular periphery in **9d**. Comparison of the H-10 and C-10 chemical shifts of **9c** and **9d** (Table II) indicates the same degree of localization of the negative charge on C-10 of both species. (b) Comparison of the NMR data of **9c** and **9d** with those of **9e** and **9f** reveals the following fundamental differences: (1) While some charge delocalization is indicated by the upfield shift of select benzenoid protons in **9e** (Figure 2) and **9f** (see the Experimental Section), the two-proton absorption of **9e** at δ 7.34 (peri hydrogens of the anthracene frame, coupled to phosphorus, J_{PH} = 12.8 Hz) and of **9f** at δ 7.24 clearly indicates the absence of any detectable paramagnetic ring current effect. (2) The carbanionic charge in phosphorus and arsenic analogues **9e** and **9f** is less localized[21] than in **9c** and **9d** as indicated by the H-10 and C-10 chemical shifts (Table II). (3) There is a significant upfield shift (by more than δ 0.25 in the case of **9e**) experienced by protons of the phenyl appendage on the heteroatom on passing from the neutral heterocycles **8e** and **8f** to the corresponding anions **9e** and **9f**.

To gain further insight into the nature of the electronic interactions between the heteroatom and the carbanionic segment in **9e** and **9f**, we undertook a ^{31}P NMR study of anion **9e** and its conjugate acid **8e**. These NMR data indicate a substantial upfield shift (δ 8.18 of the ^{31}P NMR signal on passing from neutral phosphine **8e** (δ −26.87) to anion **9e** (δ −35.05), which may be interpreted to indicate an increase in the electron density on the phosphorus atom as a result of π-electron donation by adjacent carbon atoms. On the other hand, it is clear from the published literature[22] on ^{31}P NMR spectroscopy that ^{31}P chemical shifts are subject to steric effects, and therefore the observed upfield shift could conceivably arise from steric effects accompanying **8e** → **9e** transformation.

Conformational analyses of substituted 9,10-dihydroanthracenes and their heterocyclic analogues[23] have shown that the central ring in these systems adopts the boat (or pseudoboat) conformation. Although no study regarding the conformation of **8e** or **8f** has appeared in the literature, a number of closely related systems, namely **16–20**,[24] have

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[18] Blackwell, J.; Hickinbottom, W. J. *J. Chem. Soc.* **1961**, 1405.

[19] (a) Segall, Y.; Granoth, I.; Kalir, A. *J. Chem. Soc., Chem. Commun.* **1974**, 501. (b) Segall, Y.; Alkabets, R.; Granoth, I. *J. Chem. Res. Miniprint* **1977**, 3541.

[20] Subsequent water quench of **9d–g** produced **8d–g**, respectively, in recovery yields of >75%. In the case of **9e**, a mixture of **8e** (major component) and **8g** was obtained.

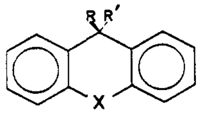
[21] This is also true in comparing **9e** and **9f** with the monoanion generated (under similar conditions) from 9,10-dihydroanthracene, which shows the carbanionic methyne NMR signal at δ 4.48 and the corresponding ^{13}C signal at δ 82.10.

[22] Gorenstein, D. G. In *Progress in Nuclear Magnetic Resonance Spectroscopy*; Emsley, J. W., Feeney, J.; Sutcliffe, L. J., Eds.; Pergamon: New York, **1984**, pp 1–98.

[23] Ternay, A. L.; Evans, S. A. *J. Org. Chem.* **1974**, *39*, 2941 and references therein.

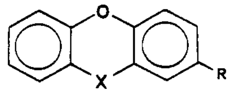
[24] (a) Compound **16**: Chen, K.-C.; Ealick, S. E.; van der Helm, D.; Barycki, J.; Berlin, K. D. *J. Org. Chem.* **1977**, *42*, 1170. (b) Compound **17**: Reference 19. (c) Compound **18**: Mann, F. G.; Millar, I. T.; Powell, H. M.; Watkin, D. J. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1384. (d) Compound **19**: Lesslie, M. S.; Turner, E. E. *J. Chem. Soc.* **1949**, 1183 and references therein. (e) Compound **20**: Mislow, K.; Zimmerman, A.; Melillo, J. T. *J. Am. Chem. Soc.* **1963**, *85*, 594.

been shown to possess folded or "butterfly" conformations. Furthermore, these structures appear to be rigid enough to practically avoid "ring fluttering" and inversion on the heteroatom.



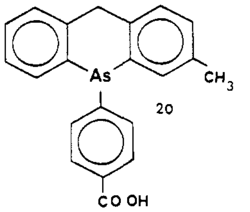
16 ; X = P-Ph, R = Me, R' = OH

17 : X = P(O)-Ph, R = Me, R' = H



18: X = P-Ph, R = H

19; X = As-Ph, R = COOH



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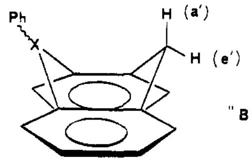
We have examined the conformation of **8e**, its oxide **8g**, and **8f** in solution by ^1H and ^{13}C NMR and have found that, at least in the case of **8e** and **8g**, these molecules exist in the rigid butterfly type conformation "B".[25] In brief, we note the following: (a) There is a chemical shift difference between two protons of the methylene group in the ^1H NMR of **8e** (δ 0.11) and **8g** (δ 0.30), indicating that the axial (a') proton is shielded[26] relative to equatorial hydrogen (e'). (b) There is a large long-range coupling of 2.94 Hz between the shielded proton (a') (δ 3.98) of the methylene group of **8g** and the aryl protons.[27] (c) In the ^{13}C NMR spectra, a large difference between the C–H coupling constants (4.1 Hz in **8e** and 11.8 Hz in **8g**) of axial (a') and equatorial (e') hydrogens is observed.



"B" ; X = P, P(O)

Referring back to the discussion of the ^{31}P NMR spectra of **8e** and **9e**, the observed upfield ^{31}P chemical shift on passing from **8e** to **9e** could be due mainly to the removal of axial (a') hydrogen in the boat conformation of **8e** and therefore a steric effect of rehybridization at the C-10 center.[28] In order to differentiate between the dominant role of steric vs electronic effects, we investigated the NMR characteristics of anion **9g**. It was expected that on passing from **9e** to **9g** the electronic demand by the heteroatomic unit would be increased substantially as a result of an increase in the electronegativity of the phosphorus atom, while the steric effect (imposed by the planarization of the C-10 center) would not change drastically.

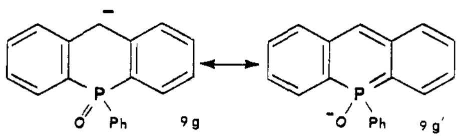
Treatment of **8g** with KNH_2 in liquid NH_3 under conditions similar to those of **8d–f** resulted in the formation of the intensely colored and thermally stable anion **9g**.[20]

Table III. ^1H, ^{13}C, and ^{31}P NMR Data for 8e–g and 9e–g[a]

compound	H-10	C-10 (J_{CH})	^{31}P
8e	3.96[b]	40.71 (130.2, 126.1)	−26.87
9e	5.08	89.24 (149.2)	−35.05
8g	4.13[b]	38.44 (137.8, 126.0)	+7.23
9g	5.58	87.50 (153.6)	+16.30

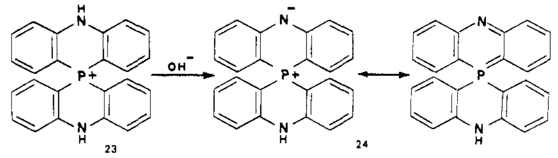
[a] All spectra recorded in liquid ammonia at 24 °C. Proton and carbon chemical shifts (δ values) are given relative to TMS and were measured from the central signal of the low-field multiplet of THF-d_8 (δ 3.7 for proton and δ 67.9 for carbon); ^{31}P chemical shifts (δ) from trimethyl phosphate as an external reference. [b] The average of the observed chemical shifts for two benzylic protons.

The key NMR data summarized in Table III contain the following informative features: (1) The methyne proton (H-10) experiences further deshielding (by ca. δ 0.50) in **9g** in comparison with the anion **9e**. The chemical shift of H-10 in **9g** is approaching the observed chemical shift of the methyne hydrogen (δ 5.75) in the closely related neutral compound **22**.[30] (2) The benzylic methyne C–H coupling constant increases substantially on passing from **9e** (J_{CH} = 149.2 Hz) to **9g** (J_{CH} = 153.6 Hz), indicating a significant increase in the "s" character of the C–H bond. (3) Concerning the ^{31}P chemical shifts, it is observed that while there is an upfield shift (ca. δ 8.18) of the ^{31}P absorption on passing from the neutral **8e** to the anion **9e**, the effect of the removal of the benzylic hydrogen is reversed for the **8g** → **9g** process. Specifically, the phosphorus chemical shift undergoes a substantial downfield shift (ca. δ 9.07) on going from the neutral **8g** to its anion **9g**. This downfield shift is in agreement with the delocalization of the negative charge onto the more electronegative oxygen and the accompanying rehybridization of P–C bonds as shown in the resonance structure **9g'**. Thus, anion **9g** behaves as a conventional phosphine oxide ylide.[29]



It is worth noting that treatment of the phosphonium salts **21** and **23** with base to yield the stable λ^5-phosphorin **22**[30] (eq 7) and the resonance-stablizied structure **24**[31] (eq 8), respectively, has been documented.

(7)



(8)

In conclusion, we note that, among the heteroanthracenide anions studied here, the selenium ion **9d** behaves similarly to paratropic sulfur analogue **9c**. The phosphorus and arsenic anions **9e** and **9f** do not exhibit any paramagnetic ring current effect. The NMR evidence presented indicates that (as in the case of sulfur and selenium anions) the carbanionic charges of **9e** and **9f** are localized to a lesser degree than those of the "first-row" heteroatom counterparts **9a** and **9b**. The major portion

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(25) The complete results of our NMR studies will be published elsewhere.

(26) In general, for structurally similar compounds, a' substitutents are shielded relative to their e' counterparts, the effect being attributed primarily to the diamagnetic anisotropic influence of the aryl rings: (a) Johnson, C. E.; Bovey, F. A. *J. Chem. Phys.* **1958**, *29*, 1012. (b) Curtin, Y.; Carlson, C. G.; McCarthy, C. G. *Can. J. Chem.* **1964**, *42*, 565.

(27) It has been shown that the greatest coupling constant results when the a' C–H bond lies perpendicular to the aromatic rings, thus allowing for efficient σ–π overlap: Lansbury, D. T.; Bieron, J. F.; Lacher, A. J. *J. Am. Chem. Soc.* **1966**, *88*, 1482.

(28) For an example, see: Orton, W. L.; Mesch, K. A.; Quin, L. D. *Phosphorus Sulfur* **1979**, *5*, 349.

(29) For examples, see: Smith, D. J. M. In *Comprehensive Organic Chemistry*; Southerland, I. O., Ed.; Pergamon: New York, 1979; p 1124.

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of this delocalization in **9e–g** involves the central ring and a significant π-electron donation to the heteroatom.

Experimental Section

Proton NMR spectra were obtained on 60-MHz Varian T-60, Mohawk 250, Bruker WM-360, and General Electric GN-500 spectrometers. ^{13}C NMR were obtained at 62.9 MHz on a Mohawk 250 spectrometer and at 125.7 MHz on a General Electric GN-500 spectrometer. ^{31}P NMR were recorded at 101.3 MHz on a Mohawk 250 spectrometer. All spectra were recorded in liquid ammonia containing tetrahydrofuran-d_8 as an internal standard. Proton and ^{13}C chemical shifts were measured from the central signal of the low-field multiplet of THF-d_8 (δ_{TMS} 3.7 for proton and δ_{TMS} 67.9 for ^{13}C). ^{31}P chemical shifts were measured (δ) from trimethyl phosphate as an external reference and are reported as positive if they are downfield from the reference signal.

Selenaxanthene (8d). Selenaxanthone was prepared from selenaphenol according to the procedures described in the literature[15a] and was reduced to selenaxanthene by the method of Urberg and Kaiser:[15b] ^{1}H NMR (60 MHz, NH_3(l)) δ 3.85 (s, 2 H), 7.0–7.80 (m, 8 H); ^{13}C NMR (62.9 MHz, NH_3(l), H-coupled) δ 43.70 (t, J = 129.2 Hz, CH_2), 127.97 (d, J = 164.4 Hz), 128.46 (d, J = 161.0 Hz), 129.61 (d, J = 163.1 Hz), 130.64 (d, J = 164.7 Hz), 132.51 (s), 139.24 (s).

9-Phenyl-9,10-dihydro-9-phosphaanthracene (8e). We prepared **8e** by way of the intermediate ketone **15**, which was synthesized according to the procedure of Granoth et al.[19] in five steps, starting with 2-bromotoluene. Reduction of ketone **15** with AlH_3 by a modified procedure of Blackwell[18] (see below) produced **8e**. The overall yield, starting with diphenylchlorophosphine (Ph_2PCl), was 19%.

Reduction of 15. Aluminum chloride (3.12 g, 23.4 mmol) was carefully dissolved in 15 mL of anhydrous ether, and the resulting solution was added dropwise to a slurry of 0.44 g (11.7 mmol) of $LiAlH_4$ in 15 mL of anhydrous ether under a nitrogen atmosphere. To the resulting gray mixture was added slowly a suspension of 1.65 g (5.73 mmol) of ketone **15**. The resulting mixture was then refluxed for 1 h. After the mixture was cooled in an ice bath, the excess $LiAlH_4$ was destroyed with wet deaerated ether. Deaerated HCl (2 M, 30 mL) was added, and after vigorous stirring, the ether layer was transferred by way of a double-tip needle and under nitrogen into a three-neck flask containing anhydrous Na_2CO_3. The aqueous layer was washed with 30 mL of deaerated ether and was combined with the previous ether layer and dried over Na_2CO_3. Filtration under N_2 and evaporation of ether at 0 °C and reduced pressure resulted in 1.20 g of a pale viscous oil, which was distilled at 155–160 °C and 0.01 mmHg to afford 1.0 g (66%) of **8e**: ^{1}H NMR (250 MHz, NH_3(l)) δ 3.91 (d, J = 17 Hz, 1 H), 4.02 (d, J = 17 Hz, 1 H), 7.27–7.72 (m, 13 H); ^{13}C NMR (62.9 MHz, NH_3(l), H-coupled) δ 40.71 (dd, J = 130.2, 126.1 Hz), 127.45–137.17, 138.9 (br s), 124.6 (br s); ^{31}P NMR (101.3 MHz, NH_3(l)) δ −26.87.

9-Phenyl-9,10-dihydro-9-phosphaanthracene 9-Oxide (8g). To a stirred solution of **8e** (0.87 g, 3.18 mmol) in 40 mL of acetone was added dropwise, at ice–water temperature, 20 mL of 30% H_2O_2. After the resultant mixture was stirred for an additional $^1/_2$ h, water (150 mL) was added and a white precipitate formed. Extraction with a total of 250 mL of $CHCl_3$ followed by drying the $CHCl_3$ solution and evaporation at reduced pressure gave 0.80 g of a viscous oil. Flash chromatography of the crude oil on silica gel using ethyl acetate–ether (1:1) as the eluent afforded **8g** [0.58 g, 63% yield; R_f 0.24, silica gel, ethyl acetate–ether (1:1)] and 9-phenyl-9,10-dihydro-9-phosphaanthracen-10-one 9-oxide[17] (0.10 g, 10%). Recrystallization of **8g** from cyclohexane–ether produced a mixture of **8g** and the above-mentioned ketone.[17] **8g**: ^{1}H NMR (500 MHz, NH_3(l)) δ 3.98 (dd, J = 18.4, 2.9 Hz, 1 H) 4.28 (d, J = 18.4 Hz, 1 H), 7.43–7.69 (m, 11 H), 8.20 (dd, J = 7.4 Hz, J_{PH} = 11.03 Hz, 2 H); ^{13}C NMR (125.8 MHz, NH_3(l), H-coupled) δ 38.44 (dd, J = 137.8, and 126.0 Hz, C-10), 128.4–136.0, 142.51 (d, J = 7.9 Hz); ^{31}P NMR (101.3 MHz, NH_3(1)) δ 7.8; MS, m/e 290 (M^+, 100), 289 (M − H, 26), 213 (M − C_6H_6, 22), 165 (M − C_6H_7PO, 38).

9,10-Dihydro-9-phenyl-9-arsaanthracene (8f). A synthesis of **8f** was formulated by Bickelhaupt et al.,[16a] but no experimental information was provided. Our synthesis of **8f** based on this formulation is as follows: The Grignard reagent prepared from o-bromodiphenylmethane[16b] was allowed to react with bis(diethylamino)chloroarsine [$(Et_2N)_2AsCl$][16c] according to a method for the phosphorus counterpart.[16d] The resulting o-[bis(diethylamino)arsino]diphenylmethane was converted to o-(dichloroarsino)diphenylmethane with dry HCl gas.[16e] Oxidation with 30% H_2O_2 in glacial acetic acid and 0 °C gave diphenylmethane-o-arsonic acid, which was converted to acridarsinic acid and then to 9-chloro-9,10-dihydro-9-arsaanthracene according to the procedure of Gump and Stolzenberg.[16e] Reaction of 9-chloro-9,10-dihydro-9-arsaanthracene with phenylmagnesium bromide according to the procedure of Jones and Mann[16f] afforded crude **8f**, which was purified by column chromatography on neutral alumina to afford pure **8f** in an overall yield of 7.4% based on o-bromodiphenylmethane. **8f**: ^{1}H NMR (60 MHz, NH_3(l)) δ 3.94 (s, 2 H), 7.17–7.7 (m, 13 H); ^{13}C NMR (62.9 MHz, NH_3(l), H-coupled) δ 42.58 (dd, J = 127.6, 127.9 Hz, C-10), 127.65–134.78, 140.0 (s), 142.8 (s); MS, m/e 318 (M^+, 57), 240 (M − C_6H_6, 75), 165 (M − C_6H_6As, 100).

Preparation of the Anions. The following procedure is typical: A medium-wall 9-in. NMR tube containing KNH_2 in liquid ammonia [prepared from ca. 50 mg, 1.28 mmol of potassium metal, ammonia (ca. 0.4 mL), and a small crystal of $FeCl_3 \cdot 6H_2O$] maintained at −78 °C was charged with a solution of selenaxanthene (**8d**; 65 mg, 0.27 mmol) in THF-d_8 (ca. 0.15 mL). A glass wool plug was pushed about half way down into the tube, and the tube was sealed under atmospheric pressure. The NMR tube was then placed in a dry ice–acetone bath at ca. −30 °C for a few minutes, and then it was inverted into a −78 °C bath, allowing the dark red solution to filter through the glass wool plug. The NMR tube was then warmed to ca. −35 °C for ca. 5 min and then to 0 °C for 5 min. The NMR spectra were recorded at probe temperature.

9d: ^{1}H NMR (360 MHz, NH_3(l)) δ 3.97 (s, 1 H), 5.59 (d, J = 8.2 Hz, 2 H), 5.64 (dd, J = 6.6, 7.4 Hz, 2 H), 6.06 (d, J = 7.4 Hz, 2 H), 6.21 (dd, J = 8.2, 6.6 Hz, 2 H); ^{13}C NMR (62.9 MHz, NH_3(l), H-coupled) δ 84.23 (d, J = 149.7 Hz, C-10), 110.01 (s, C-10b), 112.74 (d, J = 159.9 Hz), 115.41 (d, J = 157.0 Hz), 128.13 (d, J = 151.5 Hz), 128.23 (d, J = 152.7 Hz), 148.23 (s, C-10a).

9e: ^{1}H NMR (250 MHz, NH_3(l)) δ 5.08 (s, 1 H), 6.19 (tt, J = 6.9, 1.4 Hz, 2 H), 6.49 (d, J = 7.9 Hz, 2 H), 6.77 (dd, J = 7.9, 6.9 Hz, 2 H), 6.99 (m, 5 H), 7.34 (ddd, J_{PH} = 12.76 Hz, J = 7.2, 1.4 Hz, 2 H); ^{13}C NMR (62.9 MHz, NH_3(l), H-coupled) δ 89.24 (d, J = 149.2 Hz, C-10), 111.22 (s, C-10b), 111.23 (dd, J_{CH} = 158.7 Hz, J_{PC} = 16.3 Hz), 120.16 (d, J = 153.3 Hz), 126.13 (d, J = 153.3 Hz), 127.76 (d, J = 157.3 Hz), 128.59 (d, J = 153.3 Hz), 131.49 (dd, J_{CH} = 158.7 Hz, J_{PC} = 16.3 Hz), 137.12 (dd, J_{CH} = 151.9 Hz, J_{PC} = 43.4 Hz), 145.72 (br s), 149.20 (br d, J_{PC} = 30.2 Hz, C-10a); ^{31}P NMR (101.2 MHz, NH_3(l)) δ −35.05.

9f: ^{1}H NMR (250 MHz, NH_3(l)) δ 4.86 (s, 1 H), 6.04 (dt, J = 6.9, <1.0 Hz, 2 H), 6.43 (dd, J = 8.1, <1.0 Hz, 2 H), 6.69 (ddd, J = 8.1, 6.9, <1.0 Hz, 2 H), 7.07–7.12 (m, 5 H), 7.24 (dd, J = 6.9, <1.0 Hz, 2 H); ^{13}C NMR (62.9 MHz NH_3(l), H-coupled) δ 88.25 (d, J = 149.0 Hz, C-10), 110.46 (d, J = 157.0 Hz) 116.60 (s), 120.34 (d, J = 152.9 Hz), 126.78 (d, J = 157.9 Hz), 128.17 (d, J = 156.5 Hz), 128.73 (d, J = 153.0 Hz), 132.71 (d, J = 159.2 Hz), 136.68 (d, J = 150.6 Hz), 143.7 (br s), 145.35 (s).

9g: ^{1}H NMR (500 MHz, NH_3(l)) δ 5.58 (s, 1 H, 6.26 (dd, J = 5.9, 7.8 Hz, 2 H), 6.92 (dd, J = 6.8, 7.8 Hz, 2 H), 6.98 (dd, J = 5.9, 8.8 Hz, 2 H), 7.22 (dd, J = 7.8, 12.7 (PH) Hz, 2 H), 7.41–7.48 (br m, 3 H), 7.80 (dd, J = 7.8, 9.8 (PH) Hz, 2 H); ^{13}C NMR (125.8 MHz, NH_3(l), H-coupled) δ 87.50 (d, J = 153.6 Hz, C-10), 109.14 (s), 110.04 (s), 112.39 (d, J = 157.6 Hz), 124.42 (d, J = 153.6 Hz), 128.36 (d), 128.42 (d), 128.67 (d), 129.05 (d), 129.61 (d), 129.96 (d), 130.18 (d), 132.71 (d, J = 153.6 Hz), 133.68 (d, J = 157.5 Hz), 140.67 (s), 141.54 (s), 142.98 (s); ^{31}P NMR (101.3 MHz, NH_3(l)) δ +16.30.

Water (Deuterium Oxide) Quench of the Anions. The following procedure is typical: The NMR tube containing the selenaxanthenide anion (**9d**, prepared from 65 mg of **8d**) was cooled in a dry ice–acetone bath of −78 °C, and it was carefully cut open. The contents were added to a rapidly stirred solution of deuterium oxide (99.8 atom %, 15 mL) (or H_2O) and ethyl ether (85 mL) under nitrogen and at 0 °C. An immediate decolorization was observed. After the mixture was stirred for 15 min, the layers were separated, and the aqueous layer was extracted with ether

(30 mL). The combined organic layer was washed with water and saturated NaCl solution. Drying ($MgSO_4$) and removal of the solvent under reduced pressure left 58 mg of a yellow-brown solid. Recrystallization from hexane gave 50 mg (77% recovery) of crystalline **8d**: mp 143–144 °C; ^1H NMR (60 MHz, $CDCl_3$) δ 3.82 (s, 1.5 H), 6.8–7.7 (m, 8 H).

Acknowledgment. We gratefully acknowledge support of this work by the Research Corp., the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Hamilton College. We also thank the NIH Resource of Syracuse University for use of the NMR facility.

Registry No. **8d**, 261-40-5; **8e**, 59273-35-7; **8f**, 110458-53-2; **8g**, 59590-82-8; **9a**, 72301-71-4; **9d**, 110458-57-6; **9e**, 110458-58-7; **9f**, 110458-59-8; **9g**, 110458-60-1; **11**, 110458-61-2; **15**, 54086-39-4; $[(Et_2N)_2AsCl]$, 1734-99-2; KNH_2, 17242-52-3; *o*-bromodiphenylmethane, 23450-18-2; *o*-[bis(diethylamino)arsino]diphenylmethane, 110458-54-3; *o*-[bis(chloro)arsino]diphenylmethane, 110458-55-4; diphenylmethane-*o*-arsonic acid, 110458-56-5; acridarsinic acid, 5880-36-4; 9-chloro-9,10-dihydro-9-arsanthracene, 25093-02-1.

Notes

An Efficient Synthesis of Optically Pure (*S*)-(−)-3-Methylcyclohexanone

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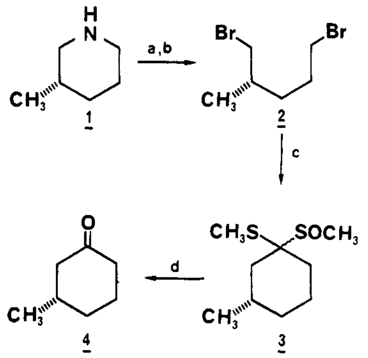
In connection with our synthetic and pharmacological studies of chiral phencyclidine analogues we required, in high optical purity, large quantities of both enantiomers of 3-methylcyclohexanone. While (+)-3-methylcyclohexanone is commercially available, its antipode is less accessible. Although a variety of synthetic methods for the preparation of the (−)-isomer have been described,[1] it was not clear that any of them could provide the optically pure material in the large quantity we required. Also, the wide range of optical rotations offered in the literature[2] for optically "pure" (+)-3-methylcyclohexanone made it difficult to assess the reliability of any of the sources, although it has been noted by Posner and Frye[3] that optically pure (+)-3-methylcyclohexanone is commercially available.[4] The importance of both (−)- and (+)-3-methylcyclohexanones as synthetic building blocks for drugs and natural products prompts us to describe the preparation of optically pure (*S*)-(−)-3-methylcyclohexanone by a route that appears amenable to large-scale synthesis and provides confirmation for the optical purity of (*R*)-(+)-3-methylcyclohexanone from a commercial source.[4]

Scheme I[a]



[a] Reagents: (a) PhCOCl, NaOH; (b) PBr_3, Br_2; (c) $CH_3SCH_2SOCH_3$, KH; (d) H_3O^+.

Ogura et al.[5] demonstrated that cyclic ketones can be prepared in a two-phase system by the dialkylation of methyl (methylsulfinyl)methyl sulfide[6] with alkyl dihalides. For this method to be applicable to the synthesis of optically active 3-methylcyclohexanones, the corresponding enantiomers of 1,5-dibromo-2-methylpentane would be needed. We prepared these enantiomers by the application of the Von Braun reaction[7] to the easily resolved optical isomers of 3-methylpiperidine.

The route to (−)-3-methylcyclohexanone is shown graphically in Scheme I. (*S*)-(−)-3-Methylpiperidine (**1**) was obtained by resolution of the racemic material according to the procedure of Marwaha et al.[8] Benzoylation and nitrogen abstraction using PBr_3/Br_2 to give (−)-2-methyl-1,5-dibromopentane (**2**) was accomplished in 46% overall yield. The reaction of **2** with methyl (methylsulfinyl)methyl sulfide in the presence of potassium hydride afforded a mixture of dithioketal *S*-oxides **3** in excellent yield. Acid hydrolysis of **3** gave rise to (*S*)-(−)-3-methylcyclohexanone (**4**) with $[\alpha]^{23}_D$ −12.8° (neat) in 83% yield. The optical purity of **4** was established by the ^1H noise-decoupled ^{13}C NMR of the cyclic ketal prepared from **4** and (2*R*,3*R*)-(−)-butane-2,3-diol.[9] It was found to be in

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(2) For example, see: (a) Eisenbraun, E. J.; McElvain, S. M. *J. Am. Chem. Soc.* **1955**, *77*, 3383. (b) Toda, F.; Tanaka, K. *J. Am. Chem. Soc.* **1983**, *105*, 5151. (c) Lightner, D. A.; Docks, E. L. *Tetrahedron* **1979**, *35*, 713. (d) Djerassi, C.; Krakower, G. W. *J. Am. Chem. Soc.* **1959**, *81*, 237. (e) See ref 1f.

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