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PREPARATION, NUCLEOPHILIC REACTIVITY, NMR, UV AND FLUORESCENCE SPECTROSCOPY, AND MATRIX PHOTOIONIZATION OF A Li-TMEDA SALT OF THE BENZOCYCLOBUT[a]ACENAPHYLENE DIANION

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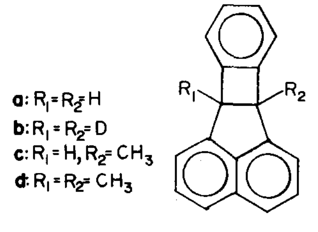
Abstract—Deprotonation of 6b,10b-dihydrobenzo[j]cyclobut[a]acenaphthylene **1a** produces a monoanion **2** or a condensed cyclobutadiene dianion **3** depending on reaction conditions. A crystalline salt of **3** was isolated and analyzed for $2Li^+$-2TMEDA-**3**. Both **2** and **3** are deuterated and methylated at the bridgehead positions. The NMR spectrum of **2** suggests exclusive delocalization of charge into the naphthalene subunit, that of **3** shows some interesting differences in charge distribution in comparison to the dianions of acenaphthylene and fluoranthene. Matrix photoionization of the dianion **3** leads reversibly to the condensed cyclobutadiene radical anion **4**, photoejection of a second electron destroys **4** irreversibly. The UV-visible spectra of **3** and **4** are compared and interpreted; **3** shows intense red fluorescence, unusual for a hydrocarbon dianion. The charge distribution in **3** and the UV-visible spectra of **3** and **4** are discussed in terms of π-electron calculations.

Some time ago we noted[1,2] that 6b,10b-dihydrobenzo[j]cyclobut[a]acenaphthylene **1a** reacts with strong bases to yield a monoanion **2** or a dianion **3**, depending on reaction conditions, and that these can be methylated to give 1c and 1d, respectively. Removal of two vicinal protons from a hydrocarbon by strong base was not well precedented at the time, but is well established now (e.g. Refs. 3, 4). The reaction is of some preparative interest for alkylations and also as a first step in an overall dehydrogenation sequence.

We have been investigating[5] the possibility that the well established technique of low-temperature matrix electron photoejection (one or two-electron oxidation of a dianion) might lead to otherwise inaccessible hydrocarbon radical anions derived from very reactive hydrocarbons and to such hydrocarbons themselves, under conditions which provide indefinite stability for spectroscopic characterization. The present paper reports details of the preparation and analysis of a crystalline salt of the polycyclic cyclobutadiene dianion **3**, and



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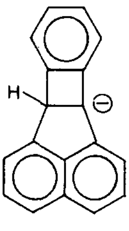

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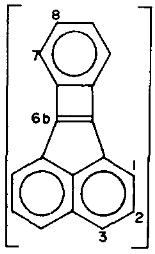

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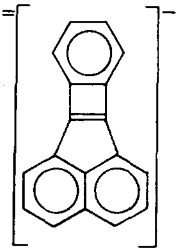

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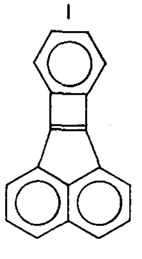

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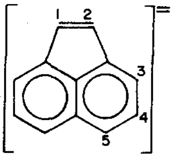

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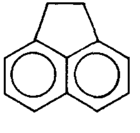

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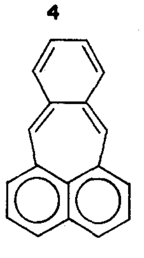

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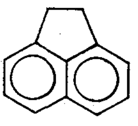

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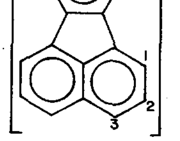

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describes some of its spectroscopic and chemical behavior. The strong fluorescence of **3** is particularly noteworthy, since hydrocarbon dianions are generally expected to photoionize easily and few have ever been reported to fluoresce.[5] We further describe the matrix photoionization **3**, which yields the radical anion **4** in the first step. Removal of a second electron has also been achieved, but is accompanied by irreversible structural changes which were not studied further.

RESULTS

Preparation of the salts of **2** *and* **3**. The course of the reaction of **1a** with strong bases is quite sensitive to reaction conditions and typically yields a mixture containing **2** and **3**. Under suitable conditions, pure **2** or **3** can be obtained. With *n*-butyllithium in 2-methyltetrahydrofuran (2-MTHF) solvent at −30°C, one obtains a yellow-orange solution ($\lambda_{max} \sim 435$ nm, 360 nm; the values reported[6] for 1-naphthylmethyllithium in THF are 498, 306 nm), and the initial NMR pattern of **1a** in 2-MTHF is gradually replaced by a more complex pattern which we attribute to **2**. Whereas **1a** shows a benzylic proton singlet at τ 4.71, a broad singlet for the benzene protons at τ 2.93, and an ABC system of the naphthalene protons in the region τ 2.1–2.9, the new pattern consists of a benzylic proton at τ 5.20, a broad singlet assigned to the protons on benzene at τ 2.92, and a complex set of peaks between τ 3.0 and τ 3.8, assigned to the naphthalene protons. This is incompletely resolved on a 60 MHz instrument and is reminiscent of the spectrum reported for 1-naphthylmethyllithium[6] (τ 2.9–4.3; the doublet centered at τ 2.35 and assigned to H_8 is missing in our case). The upfield shift of the naphthalene protons and the contrasting lack of effect on the benzene protons on going from **1a** to **2** can be rationalized as resulting from steric inhibition of efficient charge delocalization into the benzene part of the non-planar molecule **2**. Quenching with CH_3I yields **1c** and provides further support for the presence of **2**.

At room temperature, **2** slowly reacts further with excess *n*-butyllithium in 2-MTHF. The best route to pure **3** consists in reaction of **1a** with *n*-butyllithium in pentane in the presence of tetramethylethylenediamine (TMEDA). The solution briefly turns yellow, then dark red and separates purple crystals of a complex $2Li^+$-2TMEDA-**3**. These can be collected and stored in an evacuated glass tube without any apparent decomposition after a four-year period. The structure of the complex was secured by quantitative analysis (Li by atomic absorption, TMEDA and **1a** by gas chromatography), by its proton NMR spectrum (Fig. 1), and by reactions with CH_3I and D_2O which gave **1d** and **1b**, respectively.

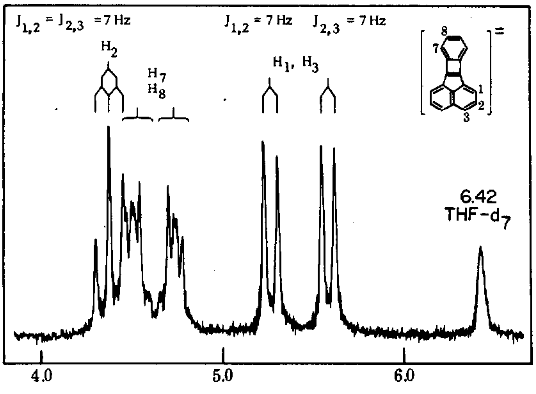

Fig. 1. Proton NMR spectrum of $2Li^+$-2TMEDA-**3** in THF-d_8 at −45° (100 MHz).

Spectroscopy of **3**. The proton NMR spectrum (Fig. 1, Table 1) allows a straightforward first-order analysis, confirmed by decoupling experiments. The low-temperature UV-visible absorption spectrum in 2-MTHF is shown in Fig. 2. The two sharp peaks at 26,500 and 27,700 cm^{-1} may correspond to two differently ion-paired species, since the lower-energy peak is absent at room temperature in a 2-MTHF and the higher-energy peak is absent at room temperature in a 2-MTHF-hexamethylphosphoramide mixture. The room-temperature spectra are relatively poorly resolved, however, and no detailed study was undertaken. At room and low temperature, solutions of **3** show bright red fluorescence whose spectral shape is independent of excitation wavelength (Fig. 2). The mirror image relation to the first absorption band and the shape of the excitation spectrum, which follows the shape of the absorption curve regardless of the wavelength at which it is monitored, leave no doubt that the emission is due to **3**.

Photoionization of **3**. By analogy to previously investigated ions,[5] one can expect electron photoejection from **3** in a rigid 2-MTHF glass (77K) to lead to **4**. Conceivably, ejection of a second electron with more energetic photons might lead to the presumably highly reactive **5** (oxidation of **3** with iodine at −80° gives a solution with transient orange color; under similar

Table 1. NMR spectra and calculated (PPP) π-electron densities in hydrocarbon dianions (THF-d_8)

Position	6b	2	1	3	7	8
3 ppm(τ)	—	4.37	5.26 5.58		~4.50 ~4.70	
q	1.242	1.064	1.183	1.230	1.122	1.131
Position	1	4	3	5	—	—
6 ppm(τ)[12]	5.54	4.96	5.50	6.70	—	—
q	1.260	1.095	1.213	1.302	—	—
Position	6b	2	1	3	7	8
10 ppm(τ)[12]	—	4.96	5.19	6.73	3.11	3.94
q	1.111	1.089	1.188	1.283	1.047	1.159

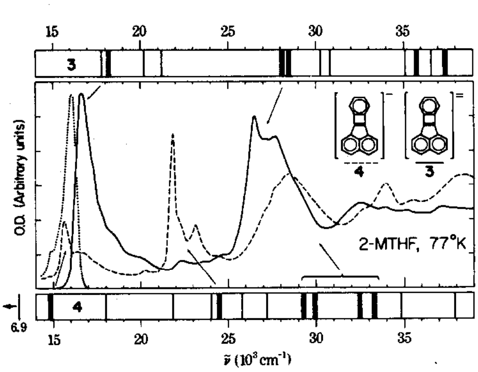

Fig. 2. *Center.* Absorption spectrum of **3** (full line) and **4** (broken line), and emission spectrum of **3** (dotted, uncorrected for instrument response) in 2-MTHF at 77K. *Top.* Calculated spectrum of **3**. *Bottom*: Calculated spectrum of **4** (thin lines, oscillator strengths, f ≤ 0.1; thick lines, f > 0.1). Assignments of observed to calculated transitions are indicated by arrows. The first calculated transition of **4** is weak and lies at 6,900 cm^{-1}.

conditions **6** smoothly gives **7**). We find that the first electron can be ionized already by long-wavelength light ($\tilde{\nu} = 16{,}400\ \mathrm{cm}^{-1}$). Formation of matrix-trapped electrons is evident from their typical near IR absorption band. Upon irradiation, the absorption spectrum of **3** gradually disappears and is replaced by a new absorption curve, with a strong peak at $21{,}800\ \mathrm{cm}^{-1}$ and several weaker peaks (Fig. 2). Simultaneously the typical easily saturated signal of free electrons and additional poorly resolved complicated structure appear in the ESR spectrum. The photoionization can be reversed and **3** reformed upon irradiation with near IR light ($\tilde{\nu} < 14{,}000\ \mathrm{cm}^{-1}$) which liberates electrons from their traps. Irradiation of a fluid solution of **3** in 2-MTHF at room temperature in the cavity of an ESR spectrometer yields a signal of total width about 30 gauss, consisting of a very large number of closely spaced poorly resolved lines which we have not been able to analyze. Similar behavior was reported and analyzed for the cyclooctatetraene dianion.[7] On the basis of the combined evidence, and by comparison with analogous previous results summarized in Ref. 5, we assign the structure of the new species as **4**.

Irradiation with light of shorter wavelengths destroys the absorption due to **4** and produces additional trapped electrons, as judged by the increase in their IR absorption band. This process is slow at $\tilde{\nu} = 29{,}400\ \mathrm{cm}^{-1}$, faster at $\tilde{\nu} = 35{,}700\ \mathrm{cm}^{-1}$; most of our work was done at $\tilde{\nu} = 39{,}400\ \mathrm{cm}^{-1}$ where an intense light source is available. General increase in background absorption is observed in the near UV and visible regions. The only recognizable new bands are quite weak and occur in the region $22{,}000$–$25{,}000\ \mathrm{cm}^{-1}$ at wavelengths corresponding to those of pleiadene[1,8] **8**. Irradiation with near IR light ($\tilde{\nu} < 14{,}000\ \mathrm{cm}^{-1}$) removes trapped electrons as evidenced by the decrease of their IR absorption band, but it does not restore the spectrum of either **4** or **3**, and produces no new strong bands. When the glass is gradually warmed up, numerous gas bubbles are formed as the glass softens, indicating the formation of a hard-to-condense poorly soluble gas, presumably H_2. Thus, the second photoionization step is clearly irreversible and involves not only electron ejection but also one or more chemical transformations, whose nature is presently not understood.

DISCUSSION

Electrophilic attack on **3**. The position of attack is 6b both in the case of methylation and deuteration, and this result stands in contrast to that reported for **6**[3] as well as **10**[9], in which initial attacks occur in positions 5 and 3, respectively. Assuming an early transition state in both of these facile reactions, reactivity should be correlated with the initial charge distribution in the dianion,[9] and the different behavior of **3** and **6** then indicates that their charge distributions are significantly different. This is in agreement with π-electron PPP calculations, and the position of highest calculated π-electron density coincides with the observed position of electrophilic attack in **3**, **6**, as well as **10** (Table 1).

Structure and NMR *spectroscopy of* **3**. The 1:1 ratio of Li^+ to TMEDA is in line with published structures of triphenylmethyllithium TMEDA[10] and lithium naphthalene dianion TMEDA[11] salts. The ^1H NMR spectrum in tetrahydrofuran-d_8 shows the expected THF-d_7 peaks at τ 6.42 and τ 8.17 and partially resolved broad TMEDA peaks near τ 7.8, as well as a series of peaks in the region τ 4–6, attributed to **3** and shown in Fig. 1. The analysis of the spectrum is straightforward except that the AA'BB' system centered τ 5.4 is not sufficiently resolved for reliable detailed study. The assignment shown in Fig. 1 and summarized in Table 1 is incomplete in that the pairs of protons 1 and 3 as well as 7 and 8 might be assigned in two possible ways. Comparison with the spectra[12] of the related dianions of acenaphthylene **6** and fluoranthene **10** shows some interesting differences (Table 1). Chemical shifts of the protons in corresponding positions in **6** and **10** are similar, only proton 3 in **6** is shifted 0.3 ppm upfield from proton 1 in **10**. On the other hand, chemical shifts of protons in **3** are quite different: protons 2 and 3 are shifted downfield, proton 8 somewhat and proton 7 very much upfield, and only proton 1 remains in the region where it was in **6** and **10**. Even though it is recognized that net charge distribution is not the only factor which determines proton chemical shifts,[13] the noticeable differences in shifts of protons in otherwise very similar environments again suggest that the π-electron distribution in **3** is significantly different from those in **6** and **10**. Qualitatively, this is not surprising considering that some resonance structures which appear quite favorable in **6** and **10** would involve a cyclobutadiene ring when drawn for **3** and thus are unlikely to contribute much. Table 1 shows that calculated π-electron densities are similar in **6** and **10** but significantly different in **3**, in a way nicely compatible with the observed differences in chemical shifts: in **3**, positions 2 and 3 have lower calculated electron densities, and position 7 a higher density compared with **6** and **10**. On the basis of the calculated densities, we favor the assignment of H_1 at τ 5.26, H_3 at τ 5.58, H_7 at τ 4.50, and H_8 at τ 4.70.

The electronic states of the dianion **3**. The spectra shown in Fig. 2 exhibit two intense absorption peaks near 16,600 and $26{,}700\ \mathrm{cm}^{-1}$ and several weak absorption bands. The location of the fluorescence curve shows that the band at $16{,}600\ \mathrm{cm}^{-1}$ undoubtedly corresponds to the lowest excited singlet state. The positions and relative intensities of the two intense absorption bands as well as those of some of the minor bands are in fairly good agreement with results of PPP calculations using standard parameters and extensive configuration interaction with doubly excited states.[14] As discussed in more detail in Ref. 14, in dianions of the size of **3** the transition energies are somewhat overestimated if one includes a total of only about a hundred configurations as we have done here. The calculation suggests that the first absorption band actually contains two almost degenerate transitions, one strong and one very weak. A standard PPP calculation using only singly excited configurations yields poorer agreement with experiment; in particular, the first strong transition is calculated at $19{,}400\ \mathrm{cm}^{-1}$, considerably above the first weak transition ($17{,}400\ \mathrm{cm}^{-1}$). Such simpler calculations generally do very well for neutral π-systems but poorly for their double anions.[14]

The electronic states of the radical anion **4**. The absorption spectrum of **4** (Fig. 2) exhibits three prominent bands near 15,700, 21,800 and $28{,}500\ \mathrm{cm}^{-1}$, and several weaker features. The locations and relative intensities of these bands are in fairly good agreement with results of standard[15] PPP calculations which are also shown in Fig. 2. This gives credence to the prediction that the first transition is located in the near IR region ($f = 0.01$), where our spectrum indeed shows an absorption, which is, however, mostly due to trapped electrons. The low-energy transition is interesting in that it should correspond to an almost pure excitation from the highest doubly occupied MO (HOMO) into the singly occupied MO (SOMO), rather than to an excitation from SOMO to the lowest free MO (LUMO) as is usual in radical anions.[15,16] The reason for this is clear from the Hückel orbital energy diagram in Fig. 3, which indicates the electronic origin of the individual transitions: HOMO and SOMO are almost degenerate, **4** is a radical anion of a biradicaloid hydrocarbon (a "highly colored" parent system of Ref. 15). In a radical anion of a "perfectly" biradicaloid hydrocarbon, HOMO and SOMO would be degenerate by symmetry, and the electronic ground state would be degenerate as well (barring a Jahn–Teller distortion from perfect symmetry). This situation occurs, for instance, in the radical anions of cyclooctatetraene and, presumably, cyclobutadiene. In a radical anion of an "imperfectly" biradicaloid hydrocarbon such as our polycyclic cyclobutadiene **4**, the orbital degeneracy is lifted, as is the ground state degeneracy, and a low-energy HOMO→SOMO transition results.

Figure 3 also shows the expected[16] relation between the spectra of **3**, **4** and **5**. Since configuration mixing plays only a secondary role for most of their transitions, these can be discussed in terms of one-electron jumps. It is seen that each transition in **3** is calculated to have a counterpart in **4** of roughly similar energy and intensity. The results suggest that the electronic origin of the 15,700 cm^{-1} band of **4** is the same as that of the 16,700 cm^{-1} band of **3**, and that the strong absorption of **4** near 28,500 cm^{-1} is similarly related to that of **3** near 26,500 cm^{-1}. On the other hand, the prominent band of **4** located at 21,800 cm^{-1} should have no analogy in the spectrum of **3**, since the calculation describes it as an electron jump into the SOMO of **4**, which already is doubly occupied in **3**. Indeed, the spectrum of **3** shows no intense band in this region (Fig. 2). Qualitative reasoning then suggests that such a band should be present in the spectrum of the neutral hydrocarbon **5**. The calculation places it at somewhat higher energies and predicts that it will be the first intense band in the absorption spectrum of **5**.

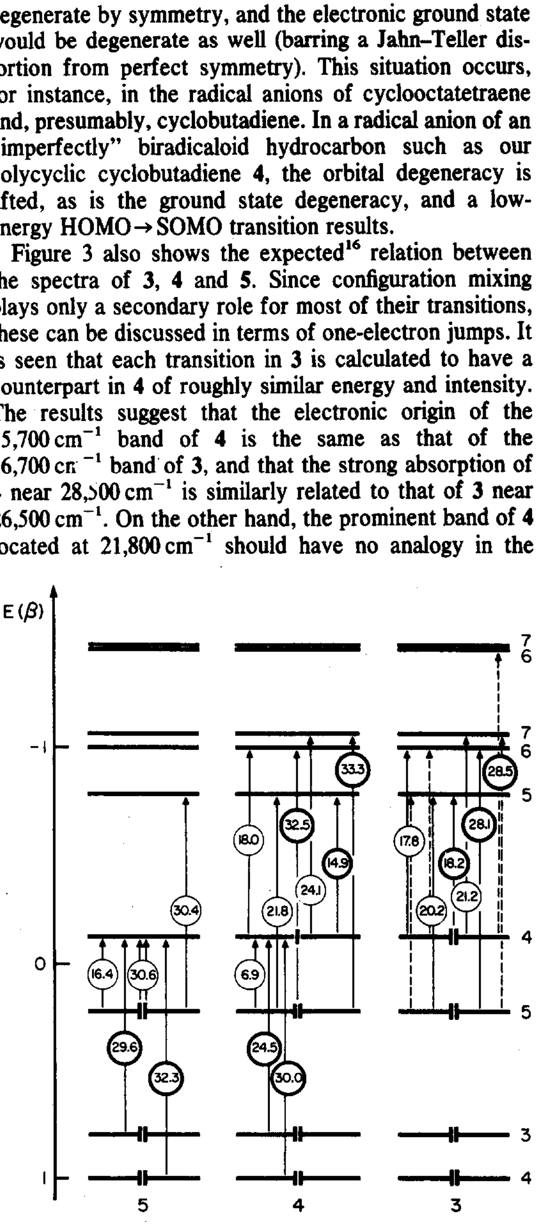

Fig. 3. Hückel orbital energies and calculated (PPP) electronic transition energies for **3**, **4** and **5** (units of 1,000 cm^{-1}, in thin circles for weak transitions, in thick circles for strong transitions), shown as arrows indicating the dominant excitation involved in the transition. Two different arrows on the same circle indicate strong configuration mixing, two identical arrows on the same circle indicate a two-electron excitation. Some additional transitions are calculated for **4** at relatively low energies (Fig. 2) but are not shown.

EXPERIMENTAL

6b - *Methyl* - 6b,10b - *dihydrobenzo*[*j*]*cyclobut*[*a*]*acenaphthylene* **1c**. A solution of **1a**[2] (114 mg, 0.5 mmole) in dry 2-MTHF (25 ml) was treated at −80° with a 2.7 M solution of *n*-butyllithium in *n*-pentane (1.0 ml, 2.7 mmole) under N_2, then warmed to −30°. After 1.5 h the NMR spectrum indicated the absence of **1a** and the presence of **2**. Excess (1.0 ml, 16 mmoles) of neat methyl iodide was added, and the stirred mixture was allowed to warm to room temp. Pentane (100 ml) was added, and the mixture washed three times with 10% aqueous HCl (10 ml) and once with water (25 ml). The organic phase was filtered and the solvent removed at reduced pressure to leave a yellowish residue which was sublimed at 100°C and 0.1 torr onto a dry-ice cooled finger, giving 60 mg of an off-white solid. This was gradient-sublimed to yield 22 mg (9%) of pure **1c**, m.p. 79–81°, and 30 mg of a mixture of **1c** and **1a**. Proton NMR spectrum (CCl_4) showed a singlet at τ 8.17 (3H), a singlet at τ 5.16 (1H), a broad peak at τ 2.92 (4H) and a multiplet centered at *ca.* τ 2.5 (6H). UV spectrum was very similar to that of **1a**. Mass spectrum showed the parent at *m*/*e* 242. Under high (>10,000) resolution the peak at nominal *m*/*e* 242 matched with PFK, 242.1086, for $C_{19}H_{14}$ calculated 242.1096.

6b,10b - *Dimethyl* - 6b,10b - *dihydrobenzo*[*j*]*cyclobut*[*a*]*acenaphthylene* **1d**. A solution of **1a** (500 mg, 2.2 mmole) in dry petroleum ether (30–60°, 150 ml) and tetramethylethylenediamine (3g, 26 mmole) was stirred and treated with 1.5 ml of a 90% solution of *n*-butyllithium in *n*-pentane under N_2. During 3 h of stirring, small purple crystals separated. The slurry was injected into a stirred solution of methyl iodide (7.1 g, 50 mmole) in dry petroleum ether (200 ml) from which last traces of moisture had been removed by addition of a few drops of *n*-butyllithium. The reaction mixture was washed twice with hydrochloric acid (10%), twice with water, the solvent was removed at reduced pressure, and the residue was sublimed at about 100° and 0.1 torr using a dry-ice cold finger vacuum sublimer, affording 220 mg of a whitish solid with a wide melting range. A portion of this material was gradient sublimed and then crystallized from absolute ethanol, m.p. 152–5°. The reaction with CH_3I can also be carried out in homogenous solution (THF). Proton NMR spectrum (CCl_4) showed a singlet at τ 8.18 (6H), a broad peak at τ 2.93 (4H), and a multiplet centered at *ca.* τ 2.6 (6H). UV spectrum was very similar to that of **1a**. Mass spectrum showed parent at *m*/*e* 256. Anal. Calc. for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.24; H, 6.32%.

6b,10b - *Dideuteriobenzo*[*j*]*cyclobut*[*a*]*acenaphthylene* **1b**. When D_2O was used for quenching of **3**, a similar workup gave **1b**, identified by its NMR spectrum (CCl_4), which was identical to that of **1a** [singlet at τ 4.70 (2H), broad peak at τ 2.95 (4H), and triplet centered at *ca.* τ 2.6 (6H)] except that the peak at τ 4.70 (2H) was absent, and by its mass spectrum (molecular ion at *m*/*e* 230, prominent peaks at *m*/*e* 228, 204, 154, 115, 114, 102).

Preparation and analysis of crystalline $2Li^{+}$-*2TMEDA*-**3** *salt.* The reaction of **1a** with TMEDA and *n*-butyllithium in *n*-pentane described above was repeated on a vacuum line using standard break-seal techniques. The crop of crystals was separated into several parts. One was used to obtain an NMR spectrum in tetrahydrofuran-d_8 (best resolution was obtained at −30°C), several were used for electronic spectroscopy and photoionization work, two were used for analysis.

A sample of the crystals (147.6 mg) was treated with deoxygenated water and *n*-hexane. The concentration of Li^{+} in the aqueous layer was determined by atomic absorption (Perkin-Elmer Model 303, Li hollow cathode lamp, 670.8 nm, air-acetylene flame). The concentration of **1a** in the hexane layer was determined by gas chromatography [Perkin–Elmer Model 900, 180 cm × 2 mm glass column, 1% QF-1 on 100/120 mesh Gas-Chrom Q, conditioned and treated with Silyl-8 (Pierce Chemical Co.), 175°, 38 ml/min N_2, retention time 3.8 min]. The concentrations of TMEDA in both aqueous and *n*-hexane phases were determined by gas chromatography (28% Pennwalt 223 GC Amine Packing and 4% KOH on 80/100 mesh Gas-Chrom R, 145°, 33 ml/min N_2, retention time 3.3 min). The results for the sample composition were 3.09% Li, 49.84% TMEDA, 47.49% **1a** (corresponding to 47.07% **3**), i.e. 105.2%, 101.3% and 98.3% of the percentage expected for $2Li^+$-2TMEDA-**3**. The high value for Li^+ may be due to occlusion of some LiOH, originating from *n*-butyl lithium and traces of moisture, on the surface of the crystals during their preparation.

Dehydrogenation of acenaphthene. A solution of acenaphthene (0.77 g, 5 mmole) in dry THF (20 ml) was stirred under N_2 at 0°C and *n*-butyllithium (1.1 ml, 90%) was added. After 1.5 h stirring at 0°, the mixture was cooled in a dry ice-acetone bath and a solution of iodine (1.3 g, 5.1 mmole) in THF (5 ml) was added dropwise. GLC analysis showed 95% acenaphthylene and 5% acenaphthene in the solution.

UV-visible and ESR spectroscopy, photoionization. Samples were prepared by vacuum-line techniques in sealed Suprasil cells (3 mm path length). The techniques and instruments used for the measurements were described in Ref. 5.

Calculations were performed as described in Ref. 15 for **4** (Longuet-Higgins–Pople SCF procedure) and as described in Ref. 14 for **3** and **5**.

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