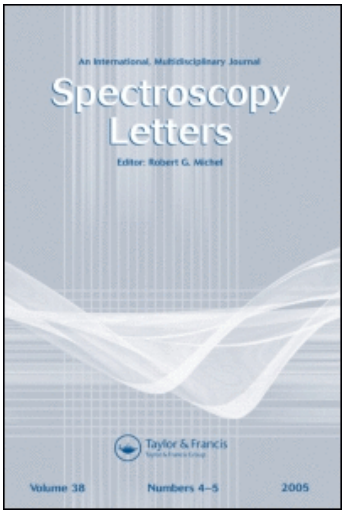

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NMR Studies of Hindered Rotation. The Diels-Alder Adduct of 4-Methyl-1, 2, 4-triazoline-3, 5-dione with Phencyclone: Restricted Motion of Unsubstituted Bridgehead Phenyls.

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NMR STUDIES OF HINDERED ROTATION. THE DIELS-ALDER ADDUCT OF 4-METHYL-1,2,4-TRIAZOLINE-3,5-DIONE WITH PHENCYCLONE: RESTRICTED MOTION OF UNSUBSTITUTED BRIDGEHEAD PHENYLS.

Key Words: Dynamic NMR, ^{1}H NMR, ^{13}C NMR, One- and two-dimensional NMR, COSY, DEPT, Restricted rotation, Stereochemistry, Anisotropy.

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ABSTRACT

4-Methyl-1,2,4-triazoline-3,5-dione was produced by lead tetraacetate oxidation of 4-methylurazole and allowed to react with phencyclone, 1. The resulting Diels-Alder adduct, 2, has been characterized by one- and two-dimensional ^{1}H and ^{13}C NMR at 300 and 75 MHz, respectively, at ambient temperatures in different solvents. The NMR data are consistent with hindered rotation of the bridgehead unsubstituted phenyl groups about the $C(sp^2)$-$C(sp^3)$ bonds, based on numbers of absorption signals in the ^{1}H and ^{13}C NMR aryl region, together with magnetic anisotropic effects in the ^{1}H spectrum. The spectral simplicity suggests further that stereochemistry at the ring junction nitrogens involves only a single isomer or very rapidly interconverting "exo"/"endo" isomers (if the ring junction nitrogens are pyramidalized).

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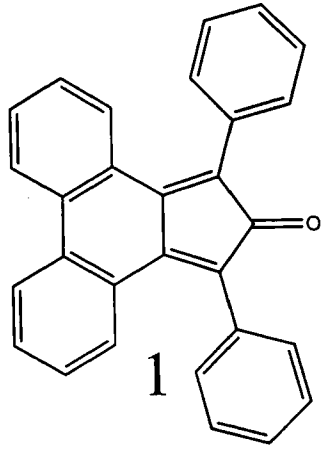
INTRODUCTION

Phencyclone, 1, can serve as a potent Diels-Alder diene for both electron-rich and electron-poor dienophiles (1). Our studies of a number of these phencyclone adducts, including those derived from norbornadiene (2,3), 1,4-benzoquinone (4), maleic anhydride (5), N-n-propylmaleimide (6), N-n-butylmaleimide (7), and N-n-carbamoylmaleimide (8), have confirmed a remarkable degree of steric hindrance. Inspection of models (9) indicates that the bridgehead phenyl ortho protons, H-2',6', could have a potential closest approach distance of as little as 0.1-0.2 Å with the phenanthrene moiety protons, H-1,8; our NMR results have suggested that this steric congestion leads to the observed slow exchange limit (SEL) spectra. The bridgehead phenyls may thus be forced into a conformation in which they are roughly perpendicular to the plane of the phenanthrene moiety (to reduce the steric repulsions noted above) and near coplanarity with the strained bridging ketone carbonyl. The adducts previously studied have exhibited some striking magnetic anisotropic effects consistent with this proposed structure.

Thus far, all of the adducts of 1 which we have prepared and examined have been derived from reaction of 1 with dienophiles corresponding to substituted ethylenes, i.e.,



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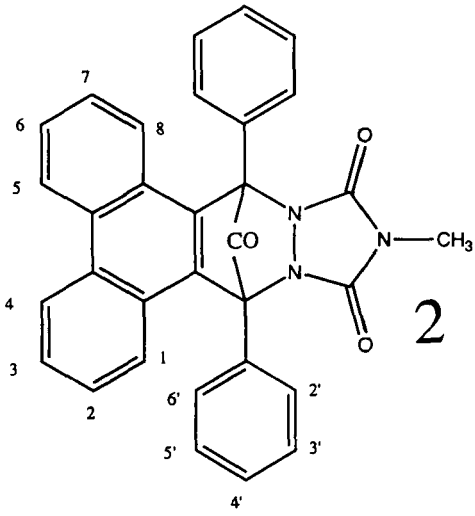

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adducts derived from C=C double bond-based dienophiles. The resulting adducts therefore have tetrahedral sp^3 carbons beta to the strained ketone carbonyl of the adduct, next to the quaternary bridgehead carbons bearing the phenyl groups. We report here the preparation of the novel adduct of 1 with 4-methyl-1,2,4-triazoline-3,5-dione, prepared by oxidation of 4-methylurazole (4-methyl-1,2,4-triazolidine-3,5-dione) with lead tetraacetate. This new adduct, 2, is derived from an azo-based (diimide) dienophile, R-N=N-R, and would therefore have trivalent ring junction nitrogens adjacent to the phenyl-bearing bridgehead carbons of the adduct. We anticipated that the incorporation of the ring junction nitrogens into this adduct, 2, could be of considerable interest with regard to: (a) potential changes in steric crowding of the bridgehead phenyls, (b) alteration of the magnetic anisotropic effects observed in previous adducts, and (c) possible stereochemistry at the ring junction nitrogens and evidence for potential interconverting isomers.

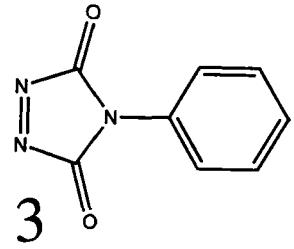
EXPERIMENTAL

General NMR and other techniques were described earlier (6,7). Spectra were obtained on a Bruker ACF300 NMR

spectrometer at 300 MHz for ^{1}H and 75 MHz for ^{13}C, at ambient temperatures (in $CDCl_3$ unless noted). Standard Bruker microprograms were ordinarily used. Reported melting points are uncorrected. IR data were obtained on a Perkin Elmer 1640 FTIR with DTGS detector. Reagents and solvents were obtained from Aldrich Chemical (Milwaukee WI) or Lancaster Synthesis (Windham NH). Synthesis of Adduct of 4-Methyltriazoline-3,5-dione with Phencyclone: 4-Methylurazole (462 mg, Lancaster, 4.01 mmol) was suspended in 60 ml CH_2Cl_2 in a 100 ml RB SN flask equipped with magnetic spin bar. The mixture was cooled in an ice-slush bath; cooling and vigorous stirring were maintained throughout the following steps until the aqueous quench and washing. Lead (IV) acetate (95%, Aldrich, 921 mg, 2.08 mmol) was added in portions during 2-3 min, resulting in progressive formation of a deep brick-red color. Phencyclone (753 mg, 1.97 mmol) was added in ca. 100 mg increments during 10 min, the transient green-black phencyclone color being discharged on stirring, eventually resulting in almost complete decolorization and a final slight yellow color. The reaction mixture was washed with water (3 x 100 ml), dried (anhyd. Na_2SO_4), and solvent was partially removed by rotary evaporator (aspirator pressure, bath temperature 35°) to a residual volume of 10 ml. Ice bath cooling and scratching with a glass rod produced fine white crystals which were collected by vacuum filtration, washed with cold CH_2Cl_2 (3 x 1 ml) and dried to yield 323 mg of the adduct (33% yield) with mp 297-298 (dec.). IR (KBr pellet, 4.0 cm^{-1} resolution, selected peaks): 1812.0, 1783.1 (strained bridging ketone CO), 1725.4 v st, 1498.3, 1448.4, 1393.8, 1167.9, 1031.1, 934.0, 763.2 st, 724.6, 696.2. (See Tables for NMR data). [Please note: 4-methyl-1,2,4-triazoline-3,5-dione is available from Aldrich.]

RESULTS AND DISCUSSION

4-Phenyl-1,2,4-triazoline-3,5-dione, 3, is an exceedingly powerful dienophile (10-15) which has commonly been prepared by oxidation of 4-phenylurazole with reagents that have included lead tetraacetate (12), t-butyl hypochlorite (10,11), activated isocyanates with dimethyl sulfoxide (14), and N-



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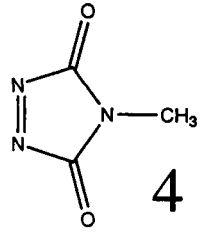
bromosuccinimide (15). The latter approach has been used to prepare other N-aryl and N-benzyl analogs (15). The possibility of different conformations or configurational isomers has been of considerable interest in various diazabicyclo[2.2.1] and [2.2.2] systems (16,17) as well as in Diels-Alder adducts of 3 (18). In these previously studied cyclic or bicyclic diaza compounds, nitrogen substituents included alkyl and carboalkoxy groups, and compounds were examined to consider possibilities of both rotational isomerism about N-C=O bonds and also potential inversions of configuration at pyramidal nitrogens. In the latter case, inversions at nonplanar nitrogens could result in "cis"-"trans" (or exo/endo) isomerism depending on the particular system. Because of the importance of these questions, we were anxious to prepare some triazolinedione-derived Diels-Alder adducts of 1, so that ring junction nitrogen configuration might be examined. Since the N-phenyl group of 3 would lead to expected ^{1}H and ^{13}C NMR spectral interferences in studies of the Diels-Alder adduct of 1, we decided to prepare the corresponding Diels-Alder adduct using the analog of 3, 4-methyl-1,2,4-triazoline-3,5-dione, 4, from the commercially



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available 4-methylurazole, using $Pb(OAc)_4$ in CH_2Cl_2 at 0-5°. The expected adduct, 2, with its N-methyl substituent, could then be examined by ^1H and ^{13}C NMR in the critical aromatic spectral regions (without N-phenyl interferences).

In the case of Diels-Alder adducts of 1 with 4-substituted-1,2,4-triazoline-3,5-diones, the question of possible configurational inversions of nonplanar ring junction nitrogens would have implications as to potential observation of endo versus exo stereochemistry of the adducts. If the nitrogens were, in fact, essentially planar rather than pyramidal, this might affect the bridgehead phenyl rotations. Phencyclone Diels-Alder adducts, like most "normal" Diels-Alder adducts, appear to preferentially form with endo stereochemistry. With sp^3 carbons formed next to the bridgehead carbons bearing the phenyls, endo adduct configuration might be expected to at least partially contribute to steric hindrance of the phenyls, since the introduced substituents would be folded back ("down") towards the phenanthrene moiety of the adduct. This might serve to further crowd the ortho H-6′ phenyl hydrogens (anti with respect of the bridging ketone carbonyl). However, in triazolinedione adducts of 1, if the ring junction nitrogens were close to planar, the remainder of the heterocyclic (triazolidinedione) ring in the adduct, i.e., the "imide"-type carbonyls, would be directed away from the phenanthrene moiety in the adduct. This could reduce the steric constraints to bridgehead phenyl rotation. Furthermore, such a change in orientation (from the endo configuration of N-alkylmaleimide adducts of 1 to the possible arrangement of 4-alkyltriazoline-3,5-dione adducts with near-planar ring junction nitrogens discussed here) might lead to observable NMR chemical shift changes. Magnetic anisotropic effects due to the two "imide"-type carbonyls in these adducts might be expected to influence the bridgehead phenyl resonances, and any changes in geometry of these carbonyls with respect to the preferred phenyl conformations would be of interest.

The ^{1}H NMR spectra of 2 were obtained in $CDCl_3$, CD_2Cl_2, and C_6D_6. Slow exchange limit (SEL) spectra could show nine distinct aryl proton signals, each of equal (2H) intensity, comprised of four gross doublets (H-1,8, H-4,5, H-2', H-6') and five gross triplets (H-2,7, H-3,6, H-3', H-4', H-5'). If the bridgehead phenyls were rotating rapidly to give fast exchange limit (FEL) spectra, only seven signals could be seen, including two "double intensity" (4H) signals, i.e., the averaged ortho protons (H-2',6', a doublet) and the averaged meta protons (H-3',5', a triplet). In addition, five (2H) signals might be expected, with two doublets for H-1,8 and H-4,5, and three triplets for H-2,7, H-3,6, and H-4'. None of the solvents employed fully separates all the signals, but an SEL system must obtain in all three solvents based on the clear presence of three 2H intensity doublets. While the $CDCl_3$ and CD_2Cl_2 spectra are quite similar, as would be expected, CD_2Cl_2 provides clean dispersion of two 2H intensity triplets, ca. 7.35-7.54 ppm, which are partly overlapped in $CDCl_3$. The C_6D_6 spectrum is radically different, reflecting substantial aromatic solvent induced shifts (ASIS), displaying three low field doublets. Only the SEL regime could be consistent with three equal intensity doublets; the expected fourth 2H intensity doublet is accidentally overlapped with other signals. The CH_3 resonance appears at 2.638, 2.602, and 1.929 ppm in $CDCl_3$, CD_2Cl_2 and C_6D_6, respectively. These results are summarized in Figure 1 and Table 1.

The proton signal assignments were established for 2 in $CDCl_3$ solution using the two-dimensional (2D) homonuclear chemical shift correlation experiment, COSY. A "high resolution" COSY90 spectrum of the aryl region showed that the lowest field doublet, assumed to be the phenanthrene moiety H-4,5, was most strongly correlated (i.e., had the most intense crosspeak) to an apparent triplet based on the 2x3 crosspeak appearance) centered at ca. 7.676 ppm, assigned as H-3,6. The strong crosspeak intensity reflects the ^{3}J vicinal coupling. A weaker crosspeak was attributed to the ^{4}J coupling to H-2,7, centered at ca. 7.377 ppm. A very weak crosspeak was assigned

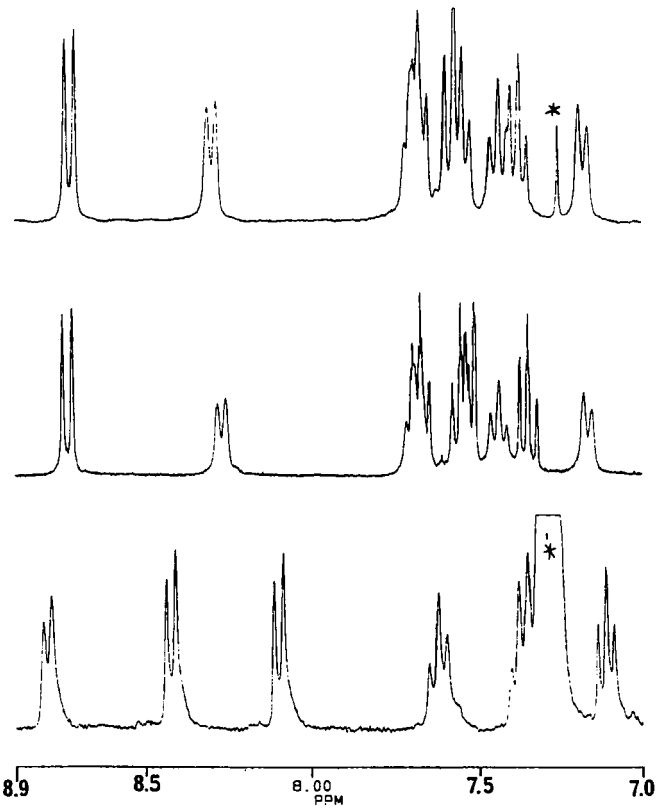

Figure 1. The 300 MHz ^1H spectrum of adduct 2 (aryl region expansions) at ambient temperatures in $CDCl_3$ (top), CD_2Cl_2 (center) and C_6D_6 (bottom). Impurities of incompletely deuterated solvent are marked with asterisks.

to the long range ^5J to H-1,8. The chemical shift for H-1,8 was centered at 7.585 ppm. Thus, all of the $(CH)_4$ spin system of the phenanthrene moiety can be directly mapped out. The doublet at 8.297 ppm is assigned to H-2', deshielded by its proximal location syn to the ketone carbonyl. This doublet shows a strong 2x3 crosspeak corresponding to ^3J vicinal coupling to H-3' at 7.691 ppm. A strong 2x2 crosspeak must be

Table 1. NMR spectral data for 2, with chemical shifts in ppm. ^1H shifts (observed coupling constants, in Hz) for 2 and selected Reference Compounds

Nucleus	2	(Est'd J, Hz)	Phenanthrene (refs. 19a, 20)
H-1,8	7.585	(7.96)	8.12
H-2,7	7.377	(7.65)	7.82
H-3,6	7.676	(7.97)	7.88
H-4,5	8.729	(8.45)	8.93
			N-Methylurazole
CH_3	2.638		3.07[a]
H-2′	8.297	(7.57)	
H-3′	7.691	(note b)	
H-4′	7.548	(7.23)	
H-5′	7.439	(7.36)	
H-6′	7.179	(7.59)	

Notes: See Results and Discussion. (a) Ref. 25, in D_2O: NH (broad) 4.92 ppm; ^{13}C peaks at 27.57 and 158.88. Data from this present work, in CD_3NO_2: NCH_3 2.98 ppm, NH (broad) ca. 7.3 ppm. (b) Data unavailable due to complexity of overlapping multiplets.

the result of ^4J "W" coupling, H-2′/6′, so that H-6′ is the high field doublet at 7.179 ppm. A weak ^4J crosspeak for H-2′/4′ is seen, permitting the assignment of H-4′ at 7.548 ppm. The long-range ^5J couplings in the phenyl rings, i.e., H-2′/5′ and H-3′/6′, are too weak to be observed; this is consistent with our earlier observations in the series of phencyclone adducts with maleimides. The chemical shift of H-5′ at 7.439 ppm follows from its strong 2x3 ^3J crosspeak with H-6′. Despite the substantial aryl proton signal overlaps in $CDCl_3$, the COSY spectrum allows extraction of distinct resonances for nine aryl protons, supporting an SEL system in 2 with hindered bridgehead phenyl rotation. COSY90 results are seen in Figure 2.

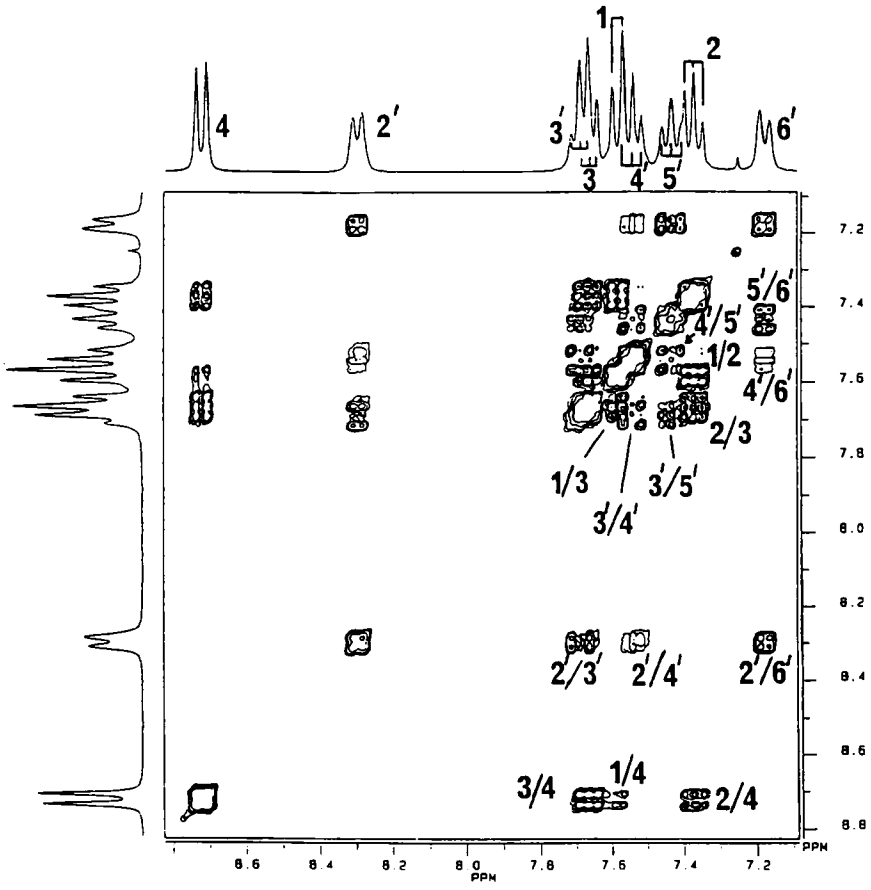

Figure 2. Two-dimensional homonuclear ^1H chemical shift correlation spectrum (COSY90) of 2, showing the expanded aryl region ("high resolution COSY"). Assignments for crosspeaks are indicated.

Use of $CDCl_3$ as solvent, despite its mediocre dispersion of aryl proton signals in 2, allows direct comparison of aryl proton chemical shifts with other phencyclone Diels-Alder adducts reported earlier. In 2, we observe a dramatic change in the relative chemical shifts of the phenanthrene moiety protons H-1 and H-2, compared to other adducts of 1, e.g., maleimide adducts (6-8). In 2, H-1 is at lower field (higher frequency) than H-2, opposite to the results of earlier described adducts. The high field position of H-1,8 in other adducts of 1 has been attributed by us to magnetic anisotropic shielding by the bridgehead phenyls, resulting from the phenyls being forced to occupy a conformation roughly perpendicular to the phenanthrene moiety in the adduct to avoid repulsions between the ortho protons H-2',6' and H-1,8. This orientation places H-1,8 of the adduct in the shielding cone of the bridgehead phenyls, leading to substantial shielding compared to the H-1,8 resonance of phenanthrene itself. For example, H-1,8 absorbed at 7.16 ppm in the adduct of 1 with N-n-butylmaleimide (7) compared to 8.12 ppm in phenanthrene. The chemical shift of H-1,8 in the adduct 2, from 1 with 4-methyl-1,2,4-triazoline-3,5-dione, could be consistent with a change in the bridgehead phenyl conformation in 2. Such a change could reflect decreased crowding of the phenyls in 2 if the bridgehead nitrogens are nearly planar, since the triazolidinedione moiety of 2 could be further from the phenyl than, e.g., the pyrrolidinedione moiety in the corresponding endo adducts obtained from 1 with N-substituted maleimides. Even a small rotation of the bridgehead phenyls in the minimum energy conformation of the adduct could have a dramatic influence on the magnitude of the anisotropic shielding of the phenanthrene moiety H-1,8. This result suggests that hindered phenyl rotation in this series of phencyclone adducts may not be exclusively due to phenyl ortho hydrogen repulsions with phenanthrene moiety H-1,8, but may additionally reflect interactions with groups attached to the bridgehead atoms beta to the ketone carbonyl. Diels-Alder adducts of 1 with 1,2,4-triazoline-3,5-dione derivatives may therefore have lower

energy barriers for bridgehead phenyl rotations than is the case in adducts derived from 1 and "substituted ethylene" dienophiles in which endo stereochemistry at carbons that are essentially tetrahedral might add to steric crowding of the phenyls.

Comparisons of ^{1}H NMR chemical shifts for the phenanthrene moiety of 2 with shifts for phenanthrene itself can suggest approximate magnitudes of the anisotropic shielding invoked above; see Table 1. For the H-1,8 position, the adduct 2 resonates about 0.54 ppm to higher field than the analogous nuclei of phenanthrene, and the H-2,7 hydrogens of adduct 2 absorb about 0.44 ppm to higher field. Less anisotropic shielding is indicated for H-3,6 and H-4,5 of 2, for these signals absorb within 0.2 ppm of the corresponding phenanthrene signals. The anisotropy of aromatic ring systems has been discussed (19b,c,21a). In contrast, the lowfield doublet at 8.297 ppm, assigned to the ortho H-2′ in 2, considered proximal and syn to the ketone carbonyl in the favored conformation, can be considered as a full 1.0 ppm to lower field than the protons of benzene, consistent with considerable deshielding anisotropy. The carbonyl anisotropy has been discussed (19d, 21b,22).

The ^{13}C NMR spectra of 2 were examined in several solvents, including $CDCl_3$, CD_2Cl_2, CD_3COCD_3 and CD_3CN, with varied relaxation delays (e.g., RD = 1, 10 or 60 sec). (Data for CD_3CN are not included here.) The different solvents were employed to obtain desired spectral dispersion in resolving all 13 aryl carbon signals possible for an SEL system of 2, while providing adequate solubility. Shorter relaxation delays lead to relatively weak responses for unprotonated carbons (quaternary, Q) including carbonyls. With a 60 sec relaxation delay (for our undegassed samples) even the quaternary carbons have a substantial fraction of the intensity of the protonated carbons, and, for example, the protonated aryl carbons can be (very roughly) quantitated. We observed that three types of aryl carbon signal were evidenced. Unprotonated versus protonated were distinguishable by the very low peak heights

and integral areas of the unprotonated carbons with short relaxation delays (e.g., RD = 1 sec). In solvents where lower solubility of 2 was observed, the unprotonated aryl carbon signals might not be discernible above noise. But with RD = 60 sec, the unprotonated carbons usually attained a substantial fraction of the peak heights (although a smaller fraction of the integrated areas) of the protonated carbons. The distinction would be unambiguously defined by DEPT45 spectra, from which the unprotonated carbon signals would be absent. But among the protonated aryl carbon signals in the usual 1D ^{13}C spectra, some signals were shorter in height while being comparable in area to the taller protonated carbon signals. The shorter, broader signals might be ascribed to the four phenyl carbons 2',6' (ortho) and 3',5'(meta). Slight line broadening could be expected if the bridgehead phenyls were undergoing a slight degree of rotation on the NMR timescale, such that the phenyl carbon resonances were not truly at the SEL, but were very slightly moved towards an intermediate exchange rate. This exchange broadening should only pertain to the four carbons of the phenyl which were off the phenyl rotation axis. C-4' (para) and C-1'(ipso) are on this axis and so would not exhibit different chemical shifts with the phenyl rotation; their signals should remain sharp, as for the phenanthrene moiety carbon signals. But the ortho and meta phenyl carbon signals exhibit different chemical shifts with the phenyl rotation, depending upon whether or not they are proximal or distal to the ketone carbonyl. These four protonated aryl carbon signals could be expected to exhibit broadening. In CD_2Cl_2 (RD = 60 sec), only twelve aryl carbon signals are seen; there is one accidental overlap at 129.8 ppm, based on the greater peak height and integrated area. Three short broad peaks are seen at 128.7, 129.3 and 130.0 ppm; we believe that the fourth broad carbon signal is overlapped with the 129.8 ppm signal. In CD_3COCD_3 (RD = 10 sec), all thirteen aryl signals are clearly recognizable above the noise. The four broad short peaks at 129.2, 129.9, 130.1 and 130.8 ppm are distinguishable by having peak heights comparable to the four

weak quaternary carbon signals while having areas comparable to the protonated carbons; the four broad peaks are also visibly broader than the other signals by the FWHM (full width at half maximum) criterion. The line broadening seems more apparent in CD_2Cl_2. In $CDCl_3$ (RD = 60 sec), only twelve aryl carbon signals are seen. Two short broad peaks are apparent at 127.9 and 128.5 ppm; we believe that the broad strong peak at 129.2 ppm represents the accidental overlap of two of the (four) broad protonated carbon signals. The 75 MHz ^{13}C NMR spectra of 2 in different solvents and a DEPT45 spectrum in $CDCl_3$ are shown in Figure 3; only the expansions of the aryl region are presented. Table 2 summarizes the ^{13}C NMR chemical shifts in different solvents, together with peak height, peak area and tentative assignment data.

Finally, we note the work of Ried and Lim (23), who reported the formation of the endo adduct from phencyclone, 1, and 4-phenyl-1,2,4-triazoline-3,5-dione, 3, on reaction in benzene at room temperature. They indicate that brief heating of this endo adduct in trichlorobenzene at 200-210° produced an isomer which they consider the exo adduct of 1 and 3. Interestingly, their endo adduct exhibits the 1780 cm^{-1} IR band which we attribute to the strained ketone carbonyl, but this band is apparently absent in their exo isomer. Unfortunately, no NMR data were presented. If distinct endo and exo Diels-Alder adducts from 1 with 3 are produced, this would clearly require stable pyramidal ring junction nitrogens in the adducts, rather than planar or rapidly equilibrating inverting nitrogens. That the ring junction nitrogens are unambiguously pyramidal in a Diels-Alder adduct of 3 (with a substituted cyclohexadiene) has been shown by x-ray structure (24). Our present NMR results have focussed on the hindered bridgehead phenyl rotations in 2 and can not rigorously define ring junction nitrogen stereochemistry. Obtention of a single main product, 2, which exhibits a single set of NMR signals, is fully consistent with endo adduct stereochemistry with pyramidal ring junction nitrogens. We are interested in exploring the behavior of 2 at elevated temperatures to examine possible endo/exo isomerism in this system.

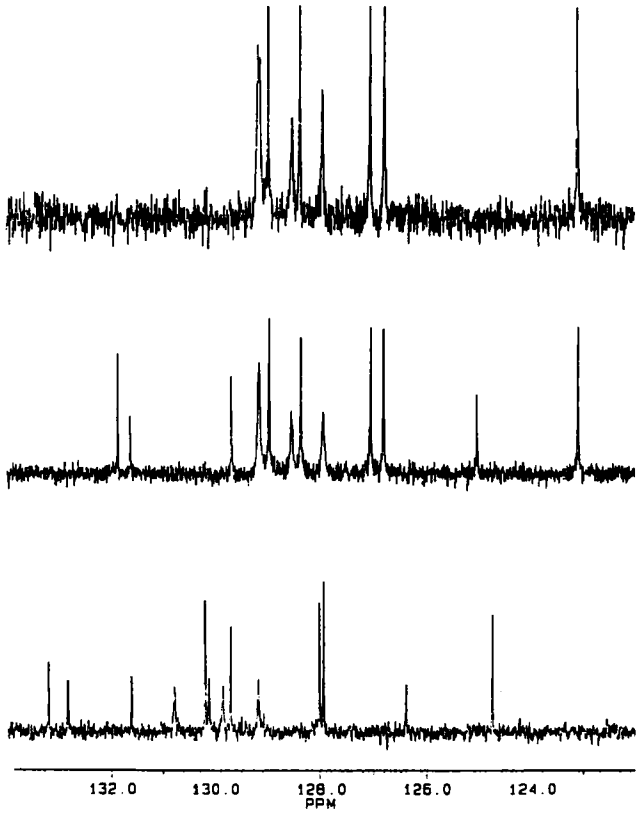

Figure 3. The 75 MHz ^{13}C NMR spectra of 2 in $CDCl_3$ and CD_3COCD_3. Only aryl region expansions are shown. DEPT45 spectrum (in $CDCl_3$) shown for comparison (top spectrum). Middle spectrum: $CDCl_3$ (relaxation delay = 3 sec, pulse width = 4 μs). Bottom spectrum: CD_3COCD_3 (relaxation delay = 10 sec, pulse width = 4μs).

CONCLUSIONS

We have oxidized 4-methyl-1,2,4-triazolidine-3,5-dione (4-methylurazole) with lead tetraacetate in CH_2Cl_2 in the presence of phencyclone, 1, to form the Diels-Alder adduct of 1 with the potent dienophile, 4-methyl-1,2,4-triazoline-3,5-dione. Ambient temperature NMR studies of the adduct, 2, were performed at 300 MHz for ^1H and 75 MHz for ^{13}C, in several

Table 2. Carbon-13 NMR shifts for adduct 2, with peak areas and heights.

$CDCl_3$[a]	Peak height[a]	Peak area[a]	Tentative assignment	Peak height[b]	Peak area[b]
186.06	1.745	1.753	bridge CO	2.245	1.130
159.41	4.091	4.406	NCO	4.345	4.808
131.88	7.051	11.675	Q	4.903	5.051
131.63	3.415	6.801	Q	4.588	5.339
129.68	5.951	12.506	Q	5.849	7.594
129.15	6.540	75.645	CH(br)x2	5.684	20.818
128.96	9.218	46.399	CH	7.510	12.477
128.53	3.731	27.703	CH(br)	3.190	8.829
128.35	8.391	43.308	CH	7.042	11.780
127.94	3.714	30.948	CH(br)	3.046	9.111
127.04	8.847	38.934	CH	6.704	10.916
126.80	8.736	43.718	CH	6.742	10.701
125.05	4.739	17.019	Q	4.780	7.475
123.09	9.069	30.298	CH	6.879	11.336
76.07	3.678	12.730	C_6H_5C	6.695	5.716
26.07	4.010	8.807	CH_3	3.707	5.407

Notes to Table 2: See Results and Discussion. The symbol Q refers to quaternary (unprotonated) aromatic carbons. These assignments are based on: relatively low peak heights and peak areas; increased peak intensities with increased relaxation delay times (RD); absence from DEPT45 spectra. Aryl carbon signals labelled br appeared relatively broad and usually exhibited areas appreciably greater than Q carbons (close to areas of the normal CH aryl peaks) but with especially low peak heights; these broad signals are tentatively assigned to C-2',3',5',6'. Note that tabulated peak heights and peak areas are raw numbers, unnormalized. For each sample (in a particular solvent, with a specified RD) the peak heights or areas may be compared, but the raw values can not be directly compared between different sample spectra. All samples were undegassed at ambient temperatures. Peak areas were obtained by manual setting of integration windows, or via the spectrometer's automated algorithm. All spectra were acquired with composite pulse decoupling (CPD) of protons. a) RD=3 sec; pulse width 4.0 μsec. The DEPT45 spectrum clearly showed two peaks near 129.15 ppm but only a single broad double intensity peak was resolved in the standard 1D ^{13}C spectrum. We believe this is a near-overlap of two broad peaks. Shifts in $CDCl_3$ are referenced to central line of solvent at 77.0 ppm.

b) Data with $CDCl_3$ solvent, RD=60 sec, pulse width 6.7 μsec. Chemical shift values were within 0.02 ppm of those in a and are not shown.

c) RD=10 sec; pulse width 4μsec. Area values with asterisk obtained by automated spectrometer algorithm, other values from manual setting of integration windows. Shifts referenced to central line of CD_3 of solvent at 30.2 ppm.

d) RD= 60 sec; pulse width 6.7 μsec. Shifts referenced to central line of CD_2Cl_2 at 54.2 ppm.
(relaxation delay = 3 sec, pulse width = 4 μs). Bottom spectrum: CD_3COCD_3 (relaxation delay = 1- sec, pulse width = 4μs).

Table 2. (continued)

CD_3COCD_3[c]	Peak height[c]	Peak area[c]	Tentative assignment	CD_2Cl_2[d]	Peak height[d]	Peak area[d]
187.83	2.268	4.28	bridge CO	187.45	0.922	0.432
160.57	3.645	8.21	NCO	160.17	1.825	1.037
133.22	5.942	21.77	Q	132.84	3.243	1.599
132.85	4.306	6.77	Q	132.38	2.682	2.057
131.61	5.089	10.16	Q	130.73	2.224	2.937
130.78	3.822	31.43	CH (br)	130.01	0.86	2.731
130.20	11.606	33.09	CH			
130.12	4.558	31.65	CH (br)	129.83	3.957	8.231
129.85	3.966	43.82	CH (br)	129.34	0.972	3.017
129.70	9.929	34.*	CH	129.14	2.800	3.528
129.16	4.647	17.38	CH (br)	128.74	1.053	3.508
128.01	11.555	27.08	CH	127.62	2.631	3.143
127.93	13.389	31.*	CH	127.53	3.391	4.289
126.39	4.438	9.89	Q	125.88	3.053	2.567
124.76	10.610	21.55	CH	124.05	3.487	3.087
77.31	3.188	5.86	C_6H_5C	76.86	2.350	1.173
26.56	6.259	10.25	CH_3	26.68	1.340	1.678

solvents. Full proton assignments were obtained in $CDCl_3$ from the COSY spectrum. In CD_3COCD_3, the aryl carbon region in the ^{13}C NMR spectrum exhibited 13 signals, consistent with slowly rotating bridgehead phenyl groups due to steric hindrance of the phenyl ortho H-2',6' with the phenanthrene moiety H-1,8. This was consistent with the ^1H NMR spectra as well. Examples of magnetic anisotropy in the ^1H spectra, including shielding of H-1,8 by the phenyls and deshielding of H-2' (proximal and syn to the ketone carbonyl), are discussed. Several significant differences in the ^1H and ^{13}C NMR spectra of 2 versus adducts of 1 with N-substituted maleimides may suggest less hindrance of the bridgehead phenyls in 2, and possible changes in adduct geometry.

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LITERATURE CITED

1. Sasaki T., Kanematsu K., Iizuka K. Molecular design by cycloaddition reactions. XXV. High peri- and regiospecificity of phencyclone. J. Org. Chem. 1976; 41 (7): 1105-1112.

2. LaPlanche L.A., Xu Y., Benshafrut R., Rothchild R., Harrison, Jr. E.A. NMR studies of hindered rotation of unsubstituted bridgehead phenyl rings in the phencyclone-norbornadiene adduct. Spectrosc. Lett. 1993; 26(1): 79-101.

3. Xu Y., LaPlanche L.A., Rothchild R. Assignment of ^{13}C resonances in the phencyclone-norbornadiene adduct via 2D NMR. ^{13}C evidence for hindered rotation of unsubstituted bridgehead phenyl rings. Spectrosc. Lett. 1993; 26(1): 179-196.

4. Callahan R., Rothchild R., Wyss H. NMR studies of hindered rotation. The Diels-Alder adduct of phencyclone with p-benzoquinone: restricted motion of bridgehead phenyls. Spectrosc. Lett. 1993; 26(9): 1681-1693.

5. Benshafrut R., Callahan R., Rothchild R. NMR studies of hindered rotation. The Diels-Alder reaction of phencyclone with maleic anhydride: restricted motion of bridgehead phenyls. Spectrosc. Lett. 1993; 26(10): 1875-1888.

6. Bynum K., Rothchild R. NMR studies of hindered rotation. The Diels-Alder adduct of phencyclone with N-n-propylmaleimide: restricted motion of bridgehead phenyls. Spectrosc. Lett. 1996; 29(8): 1599-1619.

7. Bynum K., Rothchild R. NMR studies of hindered rotation. The Diels-Alder adduct of N-n-butylmaleimide with phencyclone: restricted motion of bridgehead phenyls. Spectrosc. Lett. 1996; 29(8): 1621-1634.

8. Bynum K., Rothchild R. Analysis of hindered rotation and magnetic anisotropy by NMR. Models for drugs and agricultural compounds. The Diels-Alder adduct of phencyclone with N-carbamoylmaleimide. Spectrosc. Lett. 1997; 30(4): in press.

9. Büchi/Brinkmann stereomodels, Brinkmann Instruments, Inc., Westbury NY 11590.

10. Cookson R.C., Gilani S.S.H., Stevens I.D.R. 4-Phenyl-1,2,4-triazoline-3,5-dione: a powerful dienophile. Tetrahedron Lett. 1962; (14) 615-618.

11. Cookson R.C., Gilani S.S.H., Stevens I.D.R. Diels-Alder reactions of 4-phenyl-1,2,4-triazoline-3,5-dione. J. Chem. Soc. (C) 1967; 1905-1909.

12. Gillis B.T., Hagarty J.D. The reaction of 4-phenyl-1,2,4-triazoline-3,5-dione with conjugated dienes. J. Org. Chem. 1967; 32: 330-333.

13. Huisgen R., Elmar Konz W., Schnegg U. 1,4-Cycloaddition of azodicarboxylic phenylimide [4-phenyl-1,2,4-triazoline-3,5-dione] to cyclooctatetraene and its halogen derivatives. Angew. Chem. Int. Ed. Engl. 1972; 11(8): 715-716.

14. Moore J.A., Muth R., Sorace R. Oxidation of 4-phenylurazole with activated isocyanates and dimethyl sulfoxide. J. Org. Chem. 1974; 39(25): 3799-3800.

15. Wamhoff H., Wald K. A convenient preparation of 4-aryl-1,2,4-triazoline-3,5-diones. Org. Prep. Proc. Int. 1975; 7(5): 251-253.

16. Allred E.L., Anderson C.L., Miller R.L., Johnson A.L. The 2,3-diazabicyclo[2.2.1]heptyl ring system. IV. Cases of conformational exchange processes. Tetrahedron Lett. 1967; (6): 525-531.

17. Anderson J.E., Lehn J.M. NMR studies of rate processes and conformations - IX. Conformational rate processes in bridged bicyclic tetrahydropyridazine and piperidazine systems. Tetrahedron 1968; 24: 123-135.

18. Evnin A.B., Arnold D.R. Diels-Alder reactions of diazadienes and chemistry of the adducts. J. Amer. Chem. Soc. 1968; 90 (19): 5330-5332.

19. Günther H. NMR Spectroscopy, 2nd ed. New York: John Wiley, 1992 (a) p. 518, (b) pp. 85-93, (c) pp. 515-516, (d) pp. 82-84.

20. Haigh C.W., Mallion R.B. Proton magnetic resonance of planar condensed benzenoid hydrocarbons. I. Analysis of spectra. Mol. Phys. 1970; 18: 737-750.

21. Jackman L.M., Sternhell S. Applications of Nuclear Magnetic Resonance Spectroscopy in Organic chemistry, 2nd ed. Oxford, London, New York, etc.: Pergamon Press, 1969 (a) pp. 94-98, (b) pp. 88-92.

22. Karabatsos G.J., Sonnichsen G.C., Hsi N., Fenoglio D.J. structure by nuclear magnetic resonance. XIV. On the anisotropic effects of the carbonyl group. J. Am. Chem. Soc. 1967; 89(19): 5067-5068.

23. Ried W., Lim S.-H. Reactions with cyclopentadienones, XXVIII. 1,4-Cycloaddition of azodicarboxylic acid-phenyl imide and cyclopentadienones. Liebigs Ann. Chem. 1973; 1: 129-133.

24. Swarbrick T.M., Markó I.E., Kennard L. Tandem pericyclic reactions. Novel and efficient methodology for the rapid assembly of complex polycyclic systems. Tetrahedron Lett. 1991; 32(22): 2549-2552.

25. Pouchert C.J., Behnke J. The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra, edition I. Milwaukee WI: Aldrich Chem., 1993, 1(1),1319B.

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