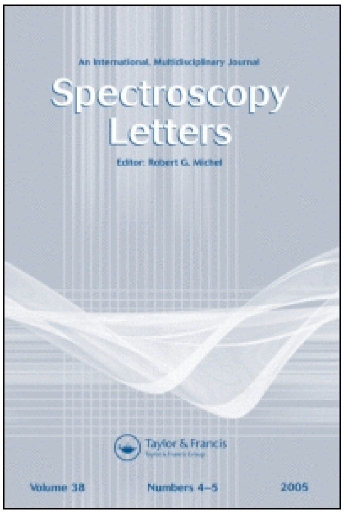

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NMR Studies of Hindered Rotation. The Diels-Alder Adduct of Phencyclone with N-n-Propylmaleimide: Restricted Motion of Bridgehead Phenyls

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NMR STUDIES OF HINDERED ROTATION. THE DIELS-ALDER ADDUCT OF PHENCYCLONE WITH N-n-PROPYLMALEIMIDE: RESTRICTED MOTION OF BRIDGEHEAD PHENYLS.

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

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ABSTRACT

The Diels-Alder adduct of phencyclone and N-n-propylmaleimide has been studied in $CDCl_3$ solution at ambient temperatures by one- and two-dimensional ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) techniques. Clear evidence is presented from slow exchange limit (SEL) spectra for hindered rotation of the bridgehead phenyls in the adduct. Full ^{1}H spectral assignments have been made via selective homonuclear decoupling and high resolution COSY experiments. The number of signals in the aryl region of ^{13}C NMR spectra also indicated slow rotation about the $C(sp^2)-C(sp^3)$ bond to the unsubstituted bridgehead phenyls.

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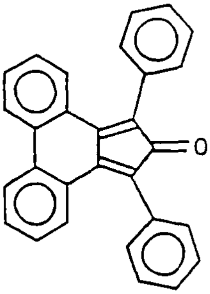
Striking evidence of magnetic anisotropic effects, seen from ^1H NMR, permits stereochemical assignment of the adduct as endo.

INTRODUCTION

In several earlier reports, we had begun to present results of NMR studies of adducts of the potent Diels-Alder diene, phencyclone, 1, with norbornadiene (1,2), 1,4-benzoquinone (3) and maleic anhydride (4). Phencyclone is unusually reactive in Diels-Alder reactions as a diene component, undergoing reaction with both electron-poor and electron-rich olefins. In the adducts described above, NMR data were consistent with a novel hindered rotation of the unsubstituted bridgehead phenyls about the C(sp^2)-C(sp^3) single bond. Here we present NMR data on the adduct of 1 with N-n-propylmaleimide, 2; the resulting Diels-Alder adduct, 3, permitted us to extend the investigations to addition compounds derived from substituted maleimides. We were interested in evaluating NMR spectral evidence of the hindered rotation in 3, determining endo versus exo stereochemistry for the Diels-Alder addition, and elaborating the ^1H NMR spectral assignments for the adduct, 3.

EXPERIMENTAL

Chloroform-d (99.8 at. % D, containing 0.03% tetramethylsilane [TMS] as internal standard) was obtained from Aldrich Chemical Corp. (Milwaukee WI 53233). N-n-Propylmaleimide was obtained from Lancaster Synthesis Inc. (Windham NH 03087) and was used as supplied without further purification. Melting points (uncorrected) were obtained on a Mel-Temp apparatus (Laboratory Devices, Cambridge MA 02139). Infrared spectra were obtained on a Perkin-Elmer 1640 Fourier transform spectrophotometer (Norwalk CT 06856). NMR data were acquired on a Bruker ACF300 spectrometer with Aspect 3000 data system and



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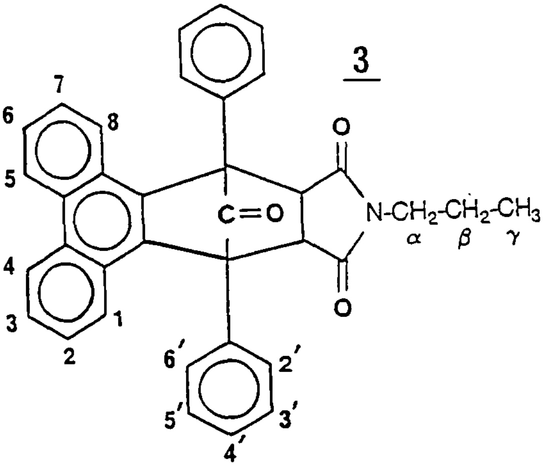
Structure 1.



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Structure 3.

array processor using the 5 mm QNP probe at ambient temperatures and thin wall NMR sample tubes. Spectra were routinely acquired with quadrature detection in the Fourier transform (FT) mode. The ^{1}H observe frequency was 300.13 MHz. Typical one-dimensional (1D) ^{1}H spectra were obtained with a spectral width of 6024 Hz (20 ppm, from ca. 15 to -5 ppm) with 16 FIDs collected in 64K complex points for a digital resolution of 0.184 Hz/point and a

5.44 s acquisition time. Pulse widths were set to 10.7 μs (90° tip angle) with zero relaxation delay. Exponential multiplication of the free induction decay (FID) with a line broadening of 0.1 Hz was used before Fourier transformation. For the 1D ^{13}C spectra, the observe frequency was 75.47 MHz. The spectral width was about 18 kHz (about 240 ppm, from 220 to -20 ppm), over 64K complex points, for a digital resolution of about 0.54 Hz/point and an acquisition time of 1.84 s. Relaxation delays were varied from 1-60s. A 6.7 μs pulse width (90° tip angle) was used. Line broadening of 0.2 Hz was applied by exponential multiplication before Fourier transformation. From 350-1340 FIDs were acquired with composite pulse decoupling of protons using a Waltz-16 sequence. The standard Bruker microprogram COSY.AU was used for homonuclear chemical shift correlation experiments, covering the full chemical shift range (ca. 9 to -0.5 ppm), or restricted to the aromatic region (ca. 9 to 6.8 ppm) for the "high resolution COSY." An example of the latter employed a spectral width of 494 Hz in F2 over 1K complex points for a digital resolution of about 1 Hz/point. COSY spectra used 256 or 512 increments in t_1, using 2 dummy scans and 16 accumulated transients for each t_1 value. A relaxation delay of 1s between pulses was used. The FIDs were processed with an unshifted sinebell window function in both dimensions. A magnitude mode transform was used. The contour plot was symmetrized about the diagonal. Data in the F1 dimension were acquired in 256 or 512 complex points and zero-filled once.

Samples of the adduct, 3, were prepared in $CDCl_3$, with concentrations from ca. 15mg/ml. Chemical shifts are reported in δ units (ppm) relative to TMS at 0.00 ppm; for ^{13}C spectra, shifts were referenced to the central line of the $CDCl_3$ triplet at 77.0

ppm. The ^1H spectrum of N-n-propylmaleimide was obtained on a Varian EM360A 60 MHz NMR spectrometer.

Preparation of Phencyclone - N-n-Propylmaleimide Adduct, 3:

Phencyclone was prepared by base-promoted condensation of dibenzylketone with 9,10-phenanthrenequinone (99+%, Aldrich) as described previously (5) using KOH in refluxing methanol. The resulting near-black, powdery 1 was used directly for reaction with 2. N-n-Propylmaleimide (152.6 mg, 1.10 mmol) was dissolved in 60 ml benzene in a 100 ml r.b. S.N. flask equipped with magnetic stirbar. Phencyclone (377.0 mg, 0.986 mmol) was added all at once to give a dark olive green opaque suspension. The flask was stoppered, protected from light (Al foil) and was stirred at ambient temperature for 0.5 hr to yield a clear pale yellow solution. Partial removal of solvent with a rotary evaporator (aspirator pressure, water bath below 40°) and cooling yielded fine white crystals of the adduct, 3, which were collected by vacuum filtration, washed with chilled portions of benzene, and sucked dry to yield 75.8 mg (14.7 % yield). This material was used without further purification: mp (dec) 257-259°. IR (KBr): 2967.7 (w), 1794.2 (s), 1702.9 (vs), 1497.6 (m), 1448.1 (m), 1436.2(m), 1395.4(m), 1382.8(w), 1361.8(m), 1351.3(m,shldr), 1325.8(w), 1291.0(w), 1222.0(m), 1198.9(m), 1164.5(w), 1134.8(m), 1070.2(w), 780.5(m), 752.8(s), 725.7(m), 701.6(s). NMR studies were performed with a solution of 15.2 mg of this material in 1 ml $CDCl_3$.

RESULTS AND DISCUSSION

The 300 MHz ^1H NMR spectrum for 3 in $CDCl_3$ is shown in Figure 1. Spectral details are summarized in Table 1. In the adducts In the adducts of phencyclone that we have previously reported, NMR data were interpreted as being consistent with SEL spectra in

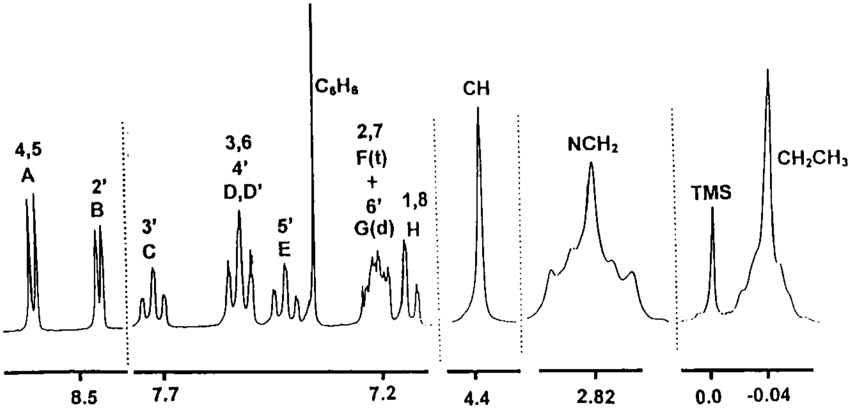

Figure 1. The 300 MHz ^1H NMR spectrum of adduct 3 in $CDCl_3$ at ambient temperatures. Note: different amplitude and chemical shift scales have been used.

Table 1. NMR spectral data for 3 (in ppm).
a) Proton chemical shifts for adduct 3 and Reference Compounds (see Notes).

Nucleus	3	Phenanthrene(ref. 7a)
H-1,8	7.15	8.12
H-2,7	7.22	7.82
H-3,6	7.52	7.88
H-4,5	8.63	8.93

	3	N-n-Propylmaleimide (note a)	
CH	4.40	6.73	(Note a: data from this present work, at 60 MHz, $CDCl_3$)
NCH_2	2.82	3.48	
$\underline{CH_2}CH_3$	-0.04	1.62	
CH_3	-0.04	0.90	
H-2'	8.40		
H-3'	7.72		
H-4'	7.52		
H-5'	7.42		
H-6'	7.22		

Table 1. (continued) b) Carbon-13 chemical shifts. (See Notes.)

δ(ppm)	Tentative assignments
196.81	C=O (ketone)
174.33	2 C=O (imide)
Aryl sp^2	
133.89	Q
133.32	Q
131.32	Q
130.94	
129.35	
129.14	
128.62	
128.39	
(128.34)	(BENZENE)
127.04	
126.61	
126.33	Q
125.83	
122.92	
ALKYL sp^3	
63.36	2 Q, <u>C</u>-C=O
44.50	2 <u>C</u>HC=O
40.43	$CH_2CH_2CH_3$
19.86	
10.48	

Notes: Chemical shifts obtained with relaxation delay of 60s; chemical shift values observed with relaxation delays of 1s or 10s were typically within 0.03 ppm of these values. "Q" denotes assignment of unprotonated quaternary aryl carbons or unprotonated bridgeheads alpha to carbonyl, based on particularly low peak heights and integrals with short relaxation delays.

which the rotations of the unsubstituted bridgehead phenyl groups were severely hindered by the hydrogens H-1,8 of the phenanthrene moiety. This appeared to be supported by examination of Dreiding stereomodels (6). The ortho hydrogens H-2′,6′ of the bridgehead phenyls would be as close as ca. 0.1 Å to H-1,8 of the phenanthrene moiety in a closest-approach conformation in which the phenyl and phenanthrene systems are roughly coplanar. Because there is a mirror plane of symmetry in 3, there are only four kinds of aryl protons on the phenanthrene system: H-1,8; H-2,7; H-3,6; and H-4,5. The phenyl rings could provide five additional sets of protons if there is slow phenyl rotation (on the NMR timescale) and the SEL regimen obtains: H-2', 3', 4', 5', 6' would each be different. The five types of phenyl protons would each have 2H intensity due to the two phenyl rings. Thus, slow phenyl rotation could lead to nine discrete 2H intensity aryl proton signals. If the phenyls spun freely for a fast exchange limit (FEL) spectrum, this would average the two ortho positions, H-2',6', with each other to give a double intensity (4H) signal; similarly, the two meta positions, H-3',5', would be interchanged by phenyl rotation and would give another 4H signal. If the gross multiplicities of these ^{1}H signals are approximated as doublets (where a single vicinal neighbor is present) as for H-1(8), 4(5), 2' and 6', or triplets (where two vicinal neighbors are present) as for H-2(7), 3(6), 3', 4', and 5', then two possible discrete spectral patterns may be expected. For SEL, four 2H doublets and five 2H triplets might be seen in the aryl region. For FEL, one 4H and two 2H doublets might be seen, in addition to one 4H and three 2H triplets. Clearly the aromatic spectral region was expected to be crucial in evaluating possible hindered rotation.

The aryl ^{1}H region showed two clear 2H intensity doublets, designated A and B, near 8.63 and 8.40 ppm, respectively. Two clear 2H "triplets" (actually triplets of doublets) are seen near 7.72 (C) and 7.42 (E) ppm. A double-intensity 4H near-triplet is seen at 7.52 ppm. An intense sharp singlet, subsequently assigned to benzene impurity, appears at 7.361 ppm. At slightly higher field are a <u>4H</u> complex multiplet centered at 7.22 ppm and a 2H distorted doublet (actually double doublet) at 7.15 ppm (H). Since this resulted in five 2H and two 4H signals (neglecting the benzene peak), which could be consistent with a "fast phenyl rotation" system, a more detailed analysis of the spectrum was called for. The highly unequal intensities of the two branches of the possible doublet (H) might merely result from distortions from first-order Pascal triangle intensities if this "doublet" were strongly spin-spin coupled to a nucleus with very similar chemical shift, i.e., in the adjacent 4H complex multiplet. But the question existed that the "doublet" (H) may have been a triplet, with the low field branch contained in the 4H multiplet. Subtractions of peak frequencies for the dd (H) gave observed ^3J couplings of 8.403 and 8.380 Hz, with the ^4J fine couplings of 1.188 and 1.165 Hz. The closest peak in the adjacent 4H multiplet (centered at 7.22 ppm) was more than 10.5 Hz away from the lowest field line of the dd (H). This exceeded the average observed vicinal couplings of ca. 8.39 Hz measured in the double doublet by substantially more than the experimental error. We therefore tentatively proceeded on the assumption that the highest field aryl multiplet, H, was a severely leaning (gross) <u>doublet</u> rather than part of a triplet. If this assumption is correct, we then have three 2H intensity doublets (A,B,H); this can only be consistent with a slowly rotating phenyl SEL system. The FEL system cannot account for three equal intensity doublets. For an SEL system to provide the observed aryl region proton spectrum, there would then be two accidental overlaps. Because of the clean, nearly 1:2:1 ratio in branch intensities of the 4H triplet at 7.52 ppm, we postulated that this represented two nearly isochronous triplets, D and D′. The complex 4H multiplet around 7.22 ppm would then be attributed to a triplet, F, and an overlapping doublet, G.

In phenanthrene itself, H-4,5 are quite deshielded, appearing at 8.93 ppm (7a). We believed that the lowest field doublet in 3 could likewise be attributed to H-4,5 of the phenanthrene moiety based on our earlier assignments with related adducts of 1 (1-4). In the COSY spectrum of 3, with a low contour level setting to more sensitively display the crosspeaks, the lowest field doublet, A, showed three crosspeaks, two strong and one weak. This defined the four spin system, $(CH)_4$, of the phenanthrene moiety. The weak crosspeak correlated the lowest field doublet, A, and the highest field doublet, H. Presumably, the weakness of the 2x2 crosspeak reflected the weak long range ^5J coupling between H-1 and H-4 of the phenanthrene moiety. The ^5J or "para" coupling is given as 0.66, 0.74 and 0.82 Hz, respectively, in benzene, naphthalene and anthracene (7b). This coupling is too small to be seen in our 1D spectrum of 3, but COSY spectra can show crosspeaks even for such small couplings (8). Somewhat surprisingly, we could not readily distinguish between the intensities of the two stronger crosspeaks correlated to doublet A. Spectral slices through the signal of A on the COSY diagonal, parallel to the axes, also failed to clearly reveal different crosspeak intensities for the stronger crosspeaks. Evidently the crosspeak correlations for the vicinal ^3J coupling, i.e., H-3/4, and the four-bond "W" coupling, i.e., ^4J, H-2/4, were comparably intense. The COSY spectrum appears in Figure 2.

The distinction as to whether the H-4,5 doublet at A was vicinal to the triplet D (coincident with a second triplet D′) or

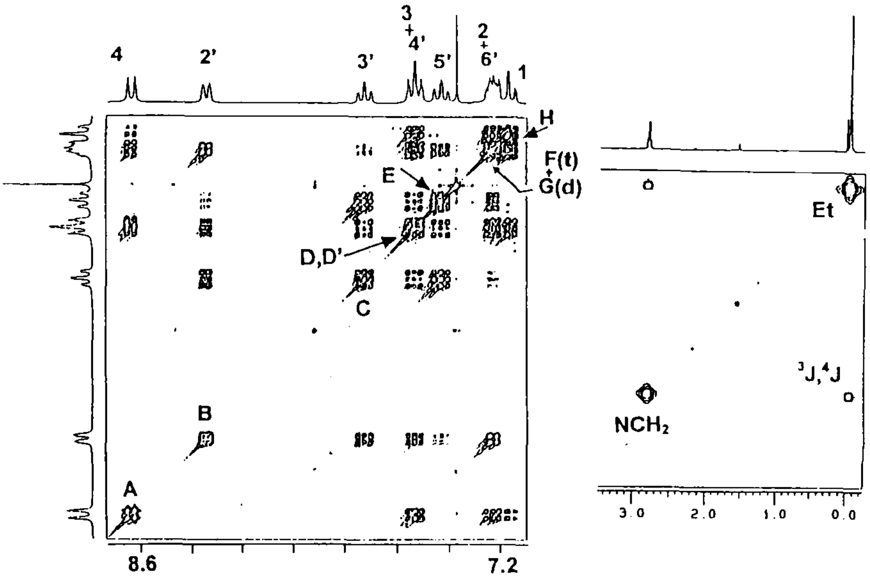

Figure 2. Two-dimensional homonuclear ^{1}H chemical shift correlation (COSY) spectrum of <u>3</u>. Preliminary and final assignments are given for diagonal contours and for the crosspeak correlations. Expanded aryl region ("high-resolution COSY") and upfield regions are shown; note different scales for contour levels and chemical shifts.

to the triplet F was made by selective homodecoupling with irradiation at A using successively greater decoupling powers. Results are shown in Figure 3. The apparent 1:2:1 triplet attributed to overlap of the two triplets D and D′ exhibits a <u>gross</u> change in appearance, becoming a highly distorted triplet with the three branches in a ratio estimated as ca. 1:4:3. This would be expected if a doublet (the expected signal of H-3 if H-4 is decoupled, leaving only H-2/3 as a source of vicinal coupling) roughly overlapped the two highfield branches of a triplet. In contrast, more subtle changes were seen in the F,G multiplet with irradiation at A. The gross shape of the F,G multiplet did not

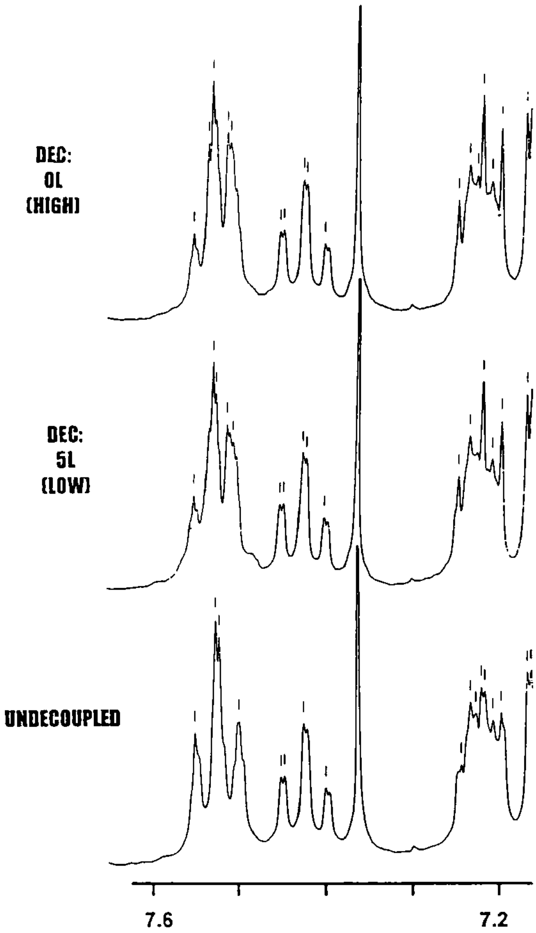

Figure 3. Selective ^1H homodecoupling spectra of 3 at increasing decoupler power. Decoupling frequency was set to the center of the lowest field doublet at 8.63 ppm.

change, and only some fine splittings seemed to be removed, presumably the ^4J "W" coupling between H-4 and H-2. The phenanthrene moiety of 3 was thus assigned as: H-4,5(A); H-3,6(D); H-2,7(F); and H-1,8(H).

With these assignments for the $(CH)_4$ spin system of the phenanthrene portion of 3, we addressed the phenyl ring assignments. With low contour level setting to sensitively observe COSY crosspeaks, the doublet B near 8.40 ppm showed two strong "2x3" crosspeaks to triplet C at 7.72 ppm and to the double intensity triplet at 7.52. If the latter triplet resulted from two overlapping triplets, D and D′, with D being part of the phenanthrene system (by our present notation), then the second coincident triplet D′ is correlated with doublet B and triplet C of the bridgehead phenyls. A third intense correlation was seen to doublet B; this was a "2x2" crosspeak with the 4H complex multiplet comprising triplet F (part of the phenanthrene moiety) and doublet G, centered at 7.22 ppm. Finally, doublet B showed a very weak correlation to the 2H triplet E at 7.42 ppm. With the observation of four crosspeaks from doublet B, we tentatively identified the five protons of the phenyl rings. The distinct 2x2 crosspeak was considered to define ^4J "W" coupling between the gross doublets expected for H-2′ and H-6′, at the ends of the $(CH)_5$ phenyl proton spin system. Since the crosspeaks B/C, B/D′, and B/G were all comparably intense, we assigned these as ^3J or ^4J couplings, with the very weak B/E crosspeak designated a ^5J <u>para</u> coupling. A comparably weak crosspeak is seen between triplet C and the doublet G. Other crosspeaks are much more intense. Thus, the very weak crosspeaks observed here are taken as demonstration of <u>para</u> ^5J couplings, both in the phenanthrene moiety H-1(8) with H-4(5), i.e., doublets A and H, and in the phenyl moiety, doublet B with triplet E, and triplet C with doublet G. This evidence for <u>para</u> orientations permits mapping the phenyl proton resonances as: B-C-D-E-G, since only in this way are ^5J <u>para</u> couplings possible to give the weak crosspeaks B/E and C/G. D shows strong crosspeaks (^3J or ^4J) to B,C,E, and G; all of the predicted ^3J or ^4J crosspeaks based on this assignment are intense. We may tentatively assign phenyl protons H-2′ as the lowfield end of the set if the bridgehead phenyls prefer a low energy conformation roughly perpendicular to the plane of the phenanthrene moiety and approximately coplanar with the bridging carbonyl. If the H-2′ protons refer to the protons "syn" to the carbonyl, significant anisotropic deshielding might be expected (9,10). In addition to carbonyl anisotropy being invoked to account for the anomalously low field position of the phenyl H-2′ hydrogens, the suggested bridgehead phenyl conformation is also consistent with the relatively high field position for the phenanthrene moiety protons H-1(8), in particular, and, to a lesser extent, the H-2(7) proton signals. In the parent hydrocarbon of phenanthrene, H-1(8) resonates rather far downfield, at 8.12 ppm, H-2(7) appears at 7.82 ppm, and H-3(6) is seen at 7.88 ppm (7a). In our assignments for <u>3</u>, H-1(8) would be at 7.15 ppm, H-2(7) at ca. 7.22 ppm and H-3(6) at 7.52 ppm. Relative to phenanthrene, H-1(8) of <u>3</u> is shielded by nearly 1.0 ppm, H-2(7) by 0.6 ppm and H-3(6) by only 0.36 ppm (the latter being a rather modest perturbation). Dreiding stereomodels suggest that this is fully consistent with the hypothesized preferred phenyl conformation. If the bridgehead phenyls are nearly perpendicular to the plane of the phenanthrene moiety in <u>3</u> to reduce repulsions between H-1(8) and the <u>ortho</u> phenyl protons, then H-1(8), 2(7) and 3(6) all lie proximal to the axis perpendicular to the plane of the phenyls and which passes through the center of the phenyl rings. These protons should therefore be subject to anisotropic shielding from the phenyl ring (9) with the relative magnitudes <u>as observed</u> based on relative distances from the bridgehead phenyls.

Outside of the aryl ^1H region, the highfield spectrum of <u>3</u> shows quite unusual chemical shifts. Aside from the 4.40 ppm 2H singlet attributed to bridgehead methines alpha to carbonyl, a 2H multiplet is seen at 2.82 ppm and a 5H multiplet at -0.04ppm, upfield of TMS. The COSY spectrum showed a strong crosspeak between the resonances at 2.82 and -0.04 ppm, but not to the 4.40 ppm signal. We have therefore assigned the 2.82 ppm signal to the NCH_2 group, with the high field 5H multiplet resulting from the CH_2CH_3 group, experiencing anisotropic shielding from the phenanthrene moiety. For the N-n-propylmaleimide itself, we observed ^1H NMR chemical shifts (in $CDCl_3$, 60MHz) of ca. 6.73 ppm (singlet) for the olefinic protons, and signals at 3.48 ppm (triplet, NCH_2), 1.62 ppm (multiplet, $C\underline{H}_2CH_3$) and 0.90 ppm (triplet, CH_3) for the n-propyl chain (see Table 1). If these values are directly compared to those in the adduct, the NCH_2 signal of the adduct is seen to resonate 0.66 ppm to higher field than in the maleimide itself. At least part of this relative shielding is probably attributable to the change from the sp^2-sp^2 carbon-carbon double bond in the maleimide to the sp^3-sp^3 carbon-carbon single bond in the Diels-Alder adduct. But for the CH_2CH_3 group, the relative shielding magnitudes are substantially greater on adduct formation. The methylene $C\underline{H}_2CH_3$ is 1.66 ppm to higher field in adduct 3, and the methyl 0.94 ppm to higher field, relative to their chemical shifts in the maleimide. If the relative shieldings in the n-propyl chain on going from the maleimide to the adduct were solely the result of electronic changes (both inductive and mesomeric effects) associated with the maleimide carbon-carbon double bond becoming a single bond, the magnitudes of the chemical shift differences (of adduct versus maleimide) should uniformly decrease as one examines signals successively further out along the n-propyl chain away from nitrogen. In fact, the differences are a maximum for the

$C\underline{H}_2CH_3$, and are larger for the methyl than for the NCH_2. This strongly argues for a through-space effect, which we attribute to magnetic shielding anisotropy experienced by the *n*-propyl group, lying in the shielding region of the phenanthrene moiety, and consistent with the *endo* stereochemistry.

There is some precedent for this shielding, as reported for the norbornadiene adduct of **1** (1,5a,11,12) in which the bridging CH_2 appears as an AB quartet, ca. +0.4 and -0.4 ppm (in $CDCl_3$). With the *N*-*n*-propyl group of **3**, we have, figuratively speaking, a meter stick in the molecule to qualitatively judge anisotropic shielding magnitudes as one moves along the *n*-propyl group from the nitrogen.

The intense singlet in the ^1H spectrum of **3** near 7.36 ppm shows essentially no crosspeak correlations in the COSY spectrum. We attribute this to impurity benzene, the reaction solvent in which the adduct **3** is prepared. Based on spectral integrations, however, the benzene may not be present in a simple stoichiometric ratio (as a solvate of crystallization); about 0.25-0.33 mole benzene appeared to be present per mole of adduct based on peak areas.

Finally, we have acquired the ^{13}C NMR spectra of **3** in $CDCl_3$ under conditions of three different relaxation delays, using values of 1, 10, and 60 sec delays between 90° pulses, with composite pulse decoupling of protons (See Figure 4). No effort was made to degas the samples or remove paramagnetic impurities. With the short relaxation delay, carbon-13 with long T_1 relaxation times, such as unprotonated carbons and small solvent molecules like benzene, should have relatively low intensity. With the longest delay employed here, the carbon spectrum acquired should be more nearly quantitative with intensities more

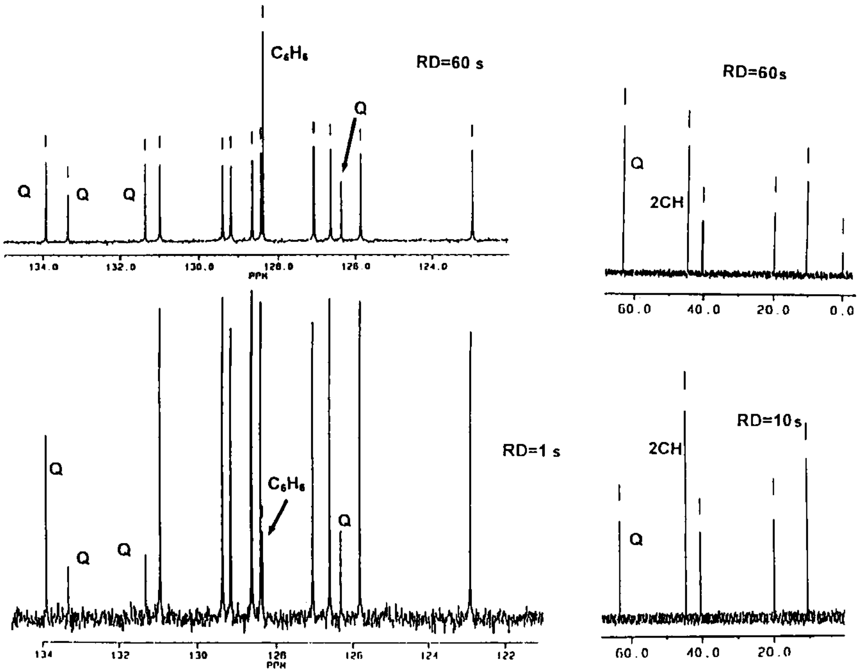

Figure 4. The 75 MHz ^{13}C NMR spectra of <u>3</u> in $CDCl_3$ (ambient temperatures) with composite pulse decoupling (CPD) for decoupling of protons. Note that intensity and chemical shift scales differ for the different regions. Relaxation delays (RD) as shown.

closely proportional to numbers of carbons. The carbon shifts are collected in Table 1. Our key interest for this present report lies in the <u>fourteen</u> signals seen in the aryl carbon region from ca. 122-135 ppm. Two of the signals are very close, nominally at 128.39 and 128.34 ppm, a separation (at 75 MHz) of less than 4 Hz. With a 1 sec relaxation delay (RD) nine of the fourteen peaks have comparable high intensities and areas. Four peaks are weak, about 30% or less of the height (or area) of the nine larger peaks. A fifth weak peak (133.9 ppm) has about 1/3 the area and 2/3 the height of the nine large peaks. The "128.34" peak is very weak. With RD = 10 sec, nine peaks remain comparably large in height (intensity) and area. The 133.9 ppm signal is equivalent in height but exhibits only 60% of the area of the nine dominant peaks. The "128.34" ppm peak is actually ca. 10% taller than the nine major peaks but has only ca. 60% of the area. Finally, with RD = 60 sec, the "128.34" ppm peak has grown to more than twice the height of any of the aryl region peaks. The other thirteen peaks have nearly equalized in height (with peaks near 133.3 and 126.3 ppm about 30-40% shorter). On the basis of this behavior, i.e. the dramatic growth in the "128.34" ppm peak as RD is increased from 1 to 60 sec, this peak is assigned as benzene. The nine major peaks are the protonated aromatic carbons C-2′,3′,4′,5′,6′ of the phenyls and C-1,2,3,4(5,6,7,8) of the phenanthrene moiety. The four remaining weak aryl carbon signals (at short RD) are the unprotonated ipso carbons C-1′ of the phenyls and the unprotonated pairs of carbons of the phenanthrene system. The lowest field, weaker carbonyl signal, ca. 196.8 ppm, would be the single ketone carbonyl, with the stronger higher field signal near 174.3 ppm assigned to the two imide carbonyls. We tentatively assign the 63.3 ppm signal as the unprotonated sp^3 bridgeheads, deshielded by carbonyl, phenyl and phenanthrene moieties, based on its dramatic growth from the RD=1 sec spectrum (lowest height and area of the five upfield carbons) to the RD=60 sec spectrum (greatest height of these signals. The four protonated carbons, with shorter relaxation times, should exhibit less intensity dependence with RD changes. We expect to present a more detailed study of ^{13}C assignments separately.

For this present work, the most significant aspect of the ^{13}C spectra is the number of signals in the aromatic region. With freely rotating bridgehead phenyls, under FEL conditions, one signal is expected for the four ortho phenyl carbons, 2′,6′, on the two phenyls. One more signal with four-carbon intensity would be expected for the meta positions, 3′,5′. Five more signals would be expected, each 2C intensity, for the four protonated positions of the phenanthrene moiety [1(8),2(7),3(6),4(5)] and the para phenyl carbons, plus four 2C intensity signals for the unprotonated aryl carbons. In summary, FEL conditions predict seven protonated carbon signals (two of which would have double intensity, i.e., four carbons) and four unprotonated carbon signals, for a total of eleven signals. In contrast, slow bridgehead phenyl rotation for SEL conditions allows for nonequivalence of C-2′ vs. C-6′, and C-3′ vs. C-5′ on the phenyl rings. Two additional signals could be seen (relative to the FEL system) for a total of thirteen. All of these thirteen correspond to two carbons each (equal intensity), with nine protonated and four unprotonated. This latter SEL situation precisely fits the actual observed spectrum. With the benzene signal clearly distinguishable based on results of experiments with varied RD, exactly thirteen aryl carbon signals are assignable to 3, with four weak (unprotonated) and nine (strong) protonated, all with comparable intensity.

CONCLUSIONS

For the Diels-Alder adduct of N-n-propylmaleimide with phencyclone, in $CDCl_3$ solution at ambient temperatures, bridgehead phenyl rotation has clearly been demonstrated to be severely hindered, with SEL spectra obtained on the 300 MHz ^1H and 75 MHz ^{13}C NMR timescales. Full ^1H assignments have been made based on 1D and 2D methods, including selective homodecoupling and COSY experiments. Interpretation of ^1H chemical shifts is consistent with bridgehead phenyl conformations roughly coplanar with the ketone carbonyl and perpendicular to the phenanthrene moiety. Magnetic anisotropic effects are invoked to account for: (a) deshielding of phenyl H-2′ (syn to the ketone carbonyl) by this carbonyl; (b) substantial shielding of phenanthrene moiety protons H-1(8) and 2(7) due to the bridgehead phenyls; (c) major shielding of the CH_2CH_3 protons of the N-n-propyl group, lying over the face of the phenanthrene moiety in the endo stereochemistry assigned to 3. Some preliminary ^{13}C assignments have been made. We plan further investigations in this series to gain further understanding of the hindered rotation process and the magnetic anisotropic geometric requirements.

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LITERATURE CITED

1. 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.

2. 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.

3. 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.

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

5. a) Harrison, Jr. E.A. Synthesis of a bicyclo[2.2.1]heptene Diels-Alder adduct. J. Chem. Educ. 1991; 68(5): 426-427; see foornote 5 therein and relevant personal communication provided by Dr. Harrison;
b) Harrison, Jr. E.A. The importance of temperature control in the preparation of phencyclone (1,3-diphenyl-2H-cyclopenta[1]phenanthrene-2-one). J. Chem. Educ. 1992; 69(7): 571; see footnote 5 therein.

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

7. Günther H. NMR Spectroscopy, 2nd ed. New York: John Wiley, 1992 (a) p. 518, (b) p. 522.

8. Derome A. Modern NMR Techniques for Chemistry Research. New York: Pergamon, 1987, pp. 227-230.

9. Jackman L.M., Sternhell S. Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, 2nd ed. Oxford, London, New York, etc.: Pergamon Press, 1969; esp. pp. 88-92 (and pp. 94-98, on aromatic rings).

10. 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.

11. Plemenkov V.V. Stereochemistry of the reaction of norbornadiene with dienes. Dokl. Akad. Nauk. SSSR 1978; 240(3): 608-611. [Chem. Abstr. 1978; 89: 107827g].

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

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