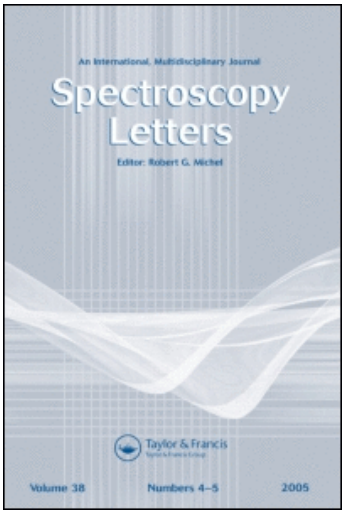


**Spectroscopy Letters**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

# NMR Studies of Hindered Rotation. The Diels-Alder Adduct of N-n-Butylmaleimide With Phencyclone: Restricted Motion of Bridgehead Phenyls

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**To cite this Article** Bynum, Kevin and Rothchild, Robert(1996) 'NMR Studies of Hindered Rotation. The Diels-Alder Adduct of N-n-Butylmaleimide With Phencyclone: Restricted Motion of Bridgehead Phenyls', Spectroscopy Letters, 29: 8, 1621 — 1634
**To link to this Article: DOI:** 10.1080/00387019608007152
**URL:** http://dx.doi.org/10.1080/00387019608007152

SPECTROSCOPY LETTERS, 29(8), 1621-1634 (1996)

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

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

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ABSTRACT

The Diels-Alder adduct of phencyclone and N-n-butylmaleimide has been prepared, and NMR studies have been carried out in $CDCl_3$ solution at ambient temperatures by one- and two-dimensional $^{1}H$ NMR (300 MHz) and $^{13}C$ NMR (75 MHz) techniques. The resulting spectra appear to be consistent with slow rotation about the hindered $C(sp^2)-C(sp^3)$ bonds to the bridgehead unsubstituted phenyls, i.e., slow exchange limit (SEL) spectra. Full rigorous $^{1}H$ spectral assignments have been made via high-resolution COSY experiments. The number of signals in the $^{13}C$ NMR aryl region were also consistent with hindered phenyl rotations; preliminary $^{13}C$ assignments are given. Striking evidence for magnetic anisotropic effects due to the phenanthrene moiety, bridging ketone carbonyl, and bridgehead phenyls are discussed, supporting endo stereochemical assignment of the adduct.

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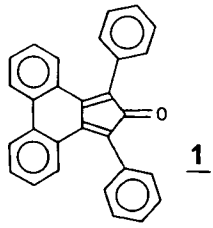
INTRODUCTION

Phencyclone, 1, the condensation product of dibenzylketone (1,3-diphenyl-2-propanone) with 9,10-phenanthrenequinone, is unusually reactive in Diels-Alder reactions as a diene component, undergoing reaction with both electron-poor and electron-rich olefins (1). We have previously observed that the Diels-Alder adducts of 1 with norbornadiene (2,3), 1,4-benzoquinone (4), and maleic anhydride (5) exhibited hindered rotation of the unsubstituted bridgehead phenyls about the $C(sp^2)-C(sp^3)$ bonds based on slow exchange limit (SEL) $^1H$ or $^{13}C$ NMR spectra. More recently, we have begun to extend these studies to phencyclone adducts of N-substituted maleimides, such as that derived from N-n-propylmaleimide (6). The maleimide adducts provide several virtues. Many different N-alkyl substituents are readily accessible which preserve the mirror-plane symmetry of the phencyclone adducts (for NMR spectral simplicity), and selection of different N-alkyl groups potentially offers a way of mapping out the magnetic anisotropic shifts in the products. Here we present the results of NMR studies on the adduct, 2, of N-n-butylmaleimide with 1.

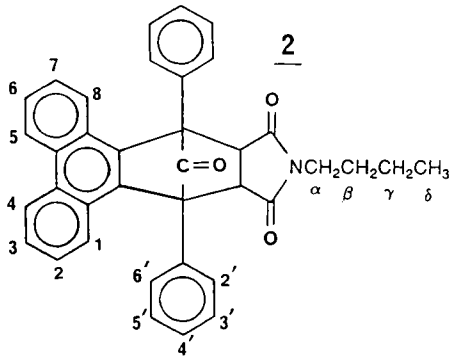
EXPERIMENTAL

Chloroform-d (99.8 at % D, containing 0.03% tetramethysilane [TMS] as internal standard) and N-n-butylmaleimide (98%) were obtained from Aldrich Chemical Co., Inc. (Milwaukee WI 53233). Phencyclone was obtained from Lancaster Synthesis Inc. (Windham NH 03087-9977). Reagents were 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 array processor using the 5mm QNP probe at ambient temperatures and thin wall NMR sample tubes. Samples were not degassed. Spectra were routinely acquired with quadrature detection in the Fourier transform (FT) mode. The $^1H$ observe frequency was 300.13 MHz. Typical one-dimensional (1D) $^1H$ spectra were obtained with a spectral width of 6024 Hz (20 ppm, from ca. 16 to -4 ppm) with 16 FIDs collected in 64K complex points for a digital resolution of 0.184 Hz/point and a 5.44s acquisition time. Pulse widths were set to 10.7 $\mu$s (90° tip




**1**

Structure 1.




**2**

Structure 2.



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 15.2 KHz (ca. 0 to 200 ppm), over 64K complex points, for a digital resolution of about 0.46 Hz/point and an acquisition time of 2.16 sec. Relaxation delays, RD, were varied from 1-60 sec. A 6.7 μs pulse width (90° tip angle) was used. Line broadening of 0.1 Hz was applied by exponential multiplication before Fourier transformation. From ca. 1500-4000 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 -1ppm) 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 535 Hz in F2 over 512 complex points for a digital resolution of about 2.1 Hz/point. COSY spectra used 128 increments in $t_1$, using two dummy scans and 8 accumulated transients for each $t_1$ value. A relaxation delay of 1 sec between pulses was used. 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 128 complex points and zero-filled once. Alternative experiments using a "COSY45" sequence resulted in somewhat less intensity of peaks on the diagonal but otherwise little difference with respect to off-diagonal crosspeaks.

Samples of the Diels-Alder adduct, 2, were prepared in $CDCl_3$. Chemical shifts are reported in $\delta$ units (ppm) relative to TMS at 0.0 ppm; for $^{13}C$ spectra, shifts were referenced to the center line of the $CDCl_3$ triplet at 77.0 ppm.

Preparation of N-n-Butylmaleimide Adduct, 2, from Phencyclone: N-n-Butylmaleimide (174.1 mg, 1.14 mmol) was dissolved in 50 ml $CH_2Cl_2$ in a 100 ml r.b. S.N. flask equipped with magnetic stirbar. Phencyclone (381.5 mg, 0.99 mmol) was added all at once to give an opaque dark olive green suspension. The flask was stoppered, protected from light by wrapping with Al foil, and stirred at ambient temperature for 1 hr to yield a clear yellow solution. Concentration to about half volume with a rotary evaporator (aspirator pressure, water bath below 40°) followed by addition of cyclohexane (10 ml) and re-concentration to half volume, with subsequent ice-slush cooling, yielded fine white crystals of the adduct, 2. The crystals were collected by vacuum filtration, washed with ice cold portions of cyclohexane (2 x 1 ml) and benzene (1x1 ml), and dried to yield 424.2 mg (79.5% yield). This material was used directly for subsequent characterization and NMR studies without further purification. The sample had mp (dec.) 266-270° and exhibited IR (KBr, $4cm^{-1}$ resolution): 3052.6 (w), 2932.0 (m), 1790.3 (st, strained C=O of ketone), 1701.4 (v. st, imide C=O), 1498.1 (m), 1447.4 (st), 1392.8 (st), 1342.3 (m), 1290.8 (w), 1222.2 (w), 1190.0 (m), 1135.7 (m), 1044.3 (w), 907.4 (w), 825.9 (w), 778.0 (st), 758.6 (st), 725.2 (st), 696.5 (st), 643.7 (w), 553.8 (w), 520.3 (w).

RESULTS AND DISCUSSION

The 300 MHz $^1$H NMR spectrum for the adduct 2 in $CDCl_3$ at ambient temperature is shown in Figure 1. The final spectral assignments and details are collected in Tables 1a and 1b. For phencyclone adducts that we have previously reported, the NMR data were considered consistent with SEL spectra, with the hindered rotations about the $C(sp^2)$-$C(sp^3)$ bonds from the unsubstituted phenyls to the bridgehead carbons resulting from severe crowding with phenanthrene moiety protons. Thus, inspection of Dreiding stereomodels (7) indicates potential closest approach distances as little as ca. 0.1-0.2 Å for the ortho hydrogens H-2′,6′ of the bridgehead phenyls relative to H-1,8 of the phenanthrene moiety. Such a situation would correspond to bridgehead phenyl conformations roughly coplanar to the phenanthrene portion of 2. To reduce this interaction, the phenyls could rotate, perhaps approaching coplanarity with the plane of the bridging ketone carbonyl as the distances from the ortho H-2′,6′ protons to H-1,8 are thereby increased. In this kind of conformation, one of the phenyl ortho protons, here designated H-2′, would be proximal to the ketone carbonyl plane, which orientation can induce downfield shifts in the H-2′ resonance due to the carbonyl magnetic anisotropy (8,9, 10b).

With hindered, slow phenyl rotation resulting in SEL spectra, the mirror plane of symmetry in 2 permits (potentially) relatively simple spectra. For $^1$H spectra, the phenanthrene moiety of 2 could result in four 2H intensity resonances, with gross doublets for H-1,8 and H-4,5, and gross triplets for H-2,7 and H-3,6 (based on the presence of one or two vicinal neighbors). With sterically hindered bridgehead phenyls rotating slowly (on the "NMR timescale") local asymmetry could result in five additional 2H intensity aryl $^1$H signals, as gross doublets for H-2′ and H-6′, and as triplets for H-3′,4′, and 5′. A total of nine 2H intensity aryl $^1$H signals could be predicted in the absence of accidental overlaps. For the $^{13}$C NMR aryl region, SEL spectra should show four protonated and three unprotonated quaternary carbon signals from the phenanthrene moiety, plus five protonated carbon signals (C-2′,3′,4′,5′,6′) and an unprotonated carbon signal (C-1′) for the phenyls, for a total of thirteen carbon signals, each corresponding to two carbons in 2. With free rotation of the bridgehead phenyls, resulting in FEL

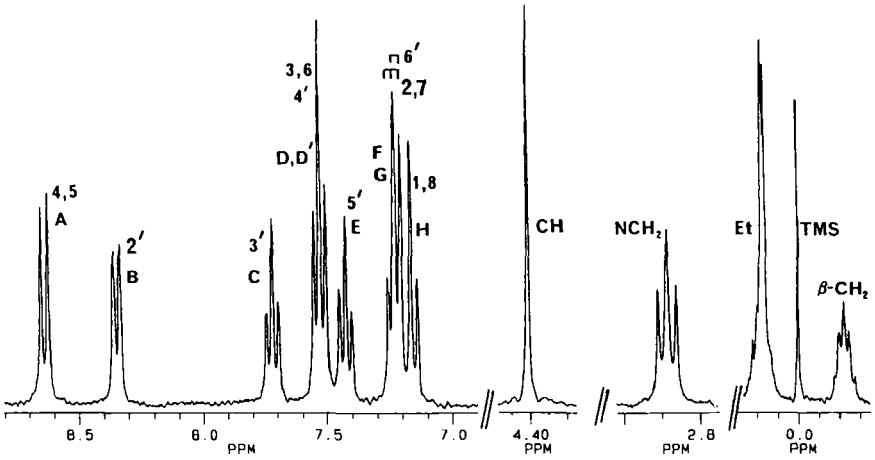



Figure 1. The 300 MHz $^1H$ spectrum of adduct 2 in $CDCl_3$ at ambient temperatures. Note that different chemical shift and amplitude scales have been used for the various spectral regions.



spectra, the phenyl ortho positions 2' and 6' are interchanged and rendered equivalent; likewise, the meta positions 3' and 5' are interchanged. As a result, the FEL aryl proton region should show a 4H intensity doublet (H-2',6') and a 4H intensity triplet (H-3',5') together with five other 2H intensity absorptions for the remaining aryl protons, for a total of seven absorption regions. The FEL $^{13}C$ aryl region should show two double intensity (i.e., 4C) protonated carbon signals for C-2',6' and C-3',5' in addition to the other carbon signals, for a total of eleven resonances. Distinguishing SEL and FEL spectra to confirm hindered phenyl rotation should therefore be straightforward for 2 and related adducts of 1, barring accidental overlaps.

For the adduct 2, the aryl $^1H$ region of the NMR spectrum showed two 2H intensity doublets centered at 8.64 ppm (J=8.44 Hz) and 8.35 ppm (J=7.76 Hz), designated as multiplets A and B, respectively. [Approximate observed splittings are shown in parentheses.] Three approximate triplets are seen, centered at 7.724 ppm (C; J=7.14 Hz); 7.529 ppm (4H intensity, D and D'; J=7.23 Hz); and 7.428 ppm (E; J=7.51 Hz). A 4H intensity gross triplet is centered near 7.23 ppm; the low intensity of the low-

field branch suggests the possibility that this multiplet results from a doublet (G) overlaying the two higher field branches of a triplet (F). Tentatively, this would correspond to the triplet (F) centered at 7.229 ppm and the doublet (G) at 7.217 ppm. A leaning doublet at ca. 7.155 ppm (J=8.25 Hz) is labeled H. That this is a true doublet is suggested by the spacing between the low-field branch of the H doublet from the high-field branch of the F/G absorptions, ca. 11.2 Hz, which is appreciably greater than expected vicinal aryl proton couplings. Some additional fine structure is apparent in these resonances. At high field are seen a 2H singlet at 4.409 ppm, 2H triplet at 2.890 ppm (J=7.38 Hz), 5H multiplet centered at 0.174 ppm, and a 2H signal (approx. quintet) at -0.223 ppm, upfield of TMS (J ca. 6.78 Hz).

Proton assignments were made, largely based on the homonuclear chemical shift correlation (COSY) spectrum shown in Figure 2. The initial assumption is that the lowest field (A) doublet is assignable to H-4,5 of the phenanthrene moiety. (This signal occurs at 8.93 ppm in the parent hydrocarbon; see Table 1a.) With low contour level setting, this doublet shows a strong crosspeak correlation to the D,D' triplets (presumably $^3J$, H-3/4), a weaker crosspeak to the F,G region (presumably $^4J$, H-2/4) and a very weak crosspeak to the highest field aryl doublet, H (assigned to $^5J$, H-1/4). These crosspeaks define the $(CH)_4$ spin system of the phenanthrene moiety. Strong crosspeaks are also seen that are assignable to H-1/2 ($^3J$) and H-2/3 ($^3J$). These assignments place H-1,8 of 2 at remarkably high field relative to the parent phenanthrene, i.e., 7.155 ppm in 2 vs. 8.12 ppm in phenanthrene. We attribute this (see below) to strong shielding magnetic anisotropy by the bridgehead phenyls in 2. The doublet B at 8.35 ppm is assigned to H-2', deshielded by near-coplanarity with the ketone carbonyl. COSY crosspeaks to this signal are assigned as due to $^3J$ ((H-2'/3') and $^4J$ (H-2'/4' and H-2'/6'). A very weak (or absent, depending on contour level setting) crosspeak corresponds to $^5J$ (H-2'/5'), protons which are para to one another on the phenyl rings. Similarly, the $^5J$ H-3'/6' crosspeak is weak or absent, and these low $^5J$ crosspeak intensities help confirm assignments. Although the $^4J$ H-2'/6' crosspeak is more intense than the H-2'/4' crosspeak, the former is distinguishable as a 2x2 crosspeak and the latter as a 2x3 crosspeak. Strong crosspeaks are also seen for H-3'/4' ($^3J$), H-

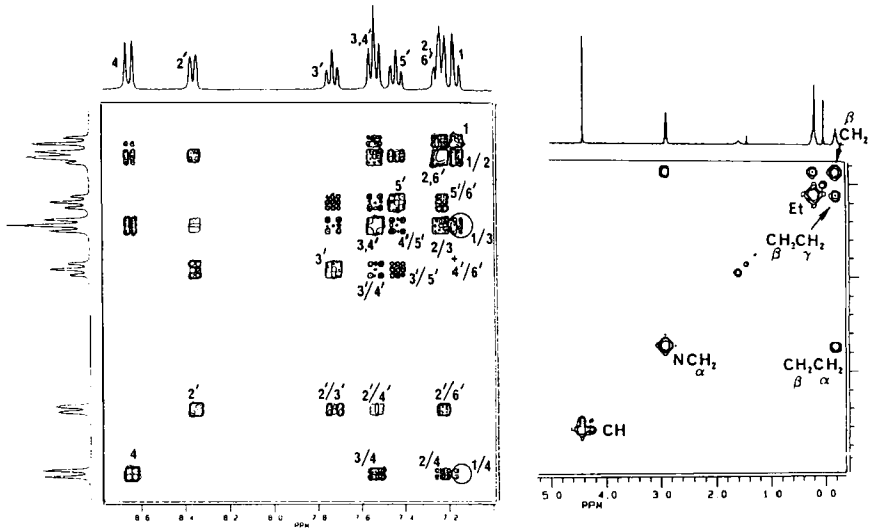



Figure 2. Two-dimensional homonuclear $^1$H chemical shift correlation spectrum (COSY) of 2. The expanded aryl region ("high-resolution COSY") and upfield regions are shown; note that different scales have been employed for chemical shifts and contour levels. Assignments for crosspeaks are indicated.

3'/5' ($^4$J), both as 3x3 crosspeaks. Thus, several of the key points used for the $^1$H assignments from COSY may be summarized as: (a) extremely weak or absent $^5$J crosspeaks for aryl para hydrogens, e.g., H-1/4; H-2'/5'; and H-3'/6'; (b) crosspeaks correlating a doublet methine from a terminus of the $(CH)_4$ spin system [of the phenanthrene moiety, H-1,8 or H-4,5] or the $(CH)_5$ spin system [of the bridgehead phenyls, H-2' or H-6'] exhibited "twofold character." When coupled to a triplet absorption (H-2,7; H-3,6, H-3',4',5'), the crosspeaks showed a 2x3 grouping. The $^4$J coupling of H-2'/6' showed a 2x2 crosspeak (for coupling between two doublets). Crosspeaks correlating couplings between triplet resonances (between non-terminal methines within the spin systems) exhibited "threefold character" with 3x3 groupings, e.g., $^4$J of H-3'/5' and $^3$J of H-3'/4' and H-4'/5'.

For the higher field signals, the 2H singlet at 4.409 ppm is assignable to the methines at the ring junction alpha to the

imide carbonyls. No crosspeaks correlate with this absorption. Only two crosspeaks are seen, one correlating the $NCH_2$ triplet at 2.89 ppm with the highest field 2H "quintet" at -0.223 ppm, assigned to the $\beta$-$CH_2$, $NCH_2\underline{CH_2}$. This crosspeak would represent $^3J$ vicinal coupling, with the $\beta$-$\underline{CH_2}$ profoundly shielded by phenanthrene moiety anisotropy, supporting endo stereochemistry in adduct 2. The 5H multiplet centered at 0.174 ppm is assigned as the coincidental overlap of the $CH_2CH_3$ protons, $\gamma$ and $\delta$ relative to the nitrogen. The remaining crosspeak seen between the 0.174 and -0.223 ppm absorptions is then attributable to $^3J$ vicinal coupling between $CH_2(\beta)$ and $CH_2(\gamma)$. We have included in Table 1a the 300 MHz $^1H$ NMR data ($CDCl_3$, ambient temperatures) for N-n-butylmaleimide, essentially first order "N+1 rule," with increasingly shielded absorptions, as expected, moving away from the electronegative nitrogen in the n-butyl group. Observed approximate multiplicities are accountable based on total numbers of vicinal protons (even if not a single magnetically equivalent set). Comparing the chemical shifts for 2 and N-n-butylmaleimide, approximate anisotropic shieldings may be calculated as being greatest for the $\beta$-$CH_2$ in 2 (1.793 ppm), followed by the $\gamma$-$CH_2$ (1.136 ppm), the $\delta$-$CH_3$ (0.753 ppm), and the $\alpha$-$\underline{N}CH_2$ (0.631 ppm). Some of the shielding in 2 versus the maleimide can be attributed to changes in electronic effects (inductive and mesomeric) on going from the $sp^2$ carbons of the HC=CH portion of the maleimide to the tetrahedral $sp^3$ methine bridgeheads in the adduct, 2.

We believe that these data imply a strong anisotropic shielding contribution from the phenanthrene moiety of 2 to an endo-oriented maleimido moiety, with maximal shielding occurring for the N-alkyl hydrogens $\beta$ and $\gamma$ to nitrogen. Smaller apparent shielding for the $NCH_2$ and the methyl in 2 may imply that these protons are not fully situated within the shielding region of the phenanthrene moiety (especially for the $NCH_2$) or are, increasingly, remote from the position of maximal anisotropic shielding (for the methyl). Shielding of phenanthrene moiety protons in 2 versus phenanthrene itself seems to correlate qualitatively with expected shielding magnitudes resulting from bridgehead phenyl conformations roughly perpendicular to the phenanthrene moiety plane. Models suggest that this arrangement would place H-1,8 of 2 squarely within the shielding cones of the

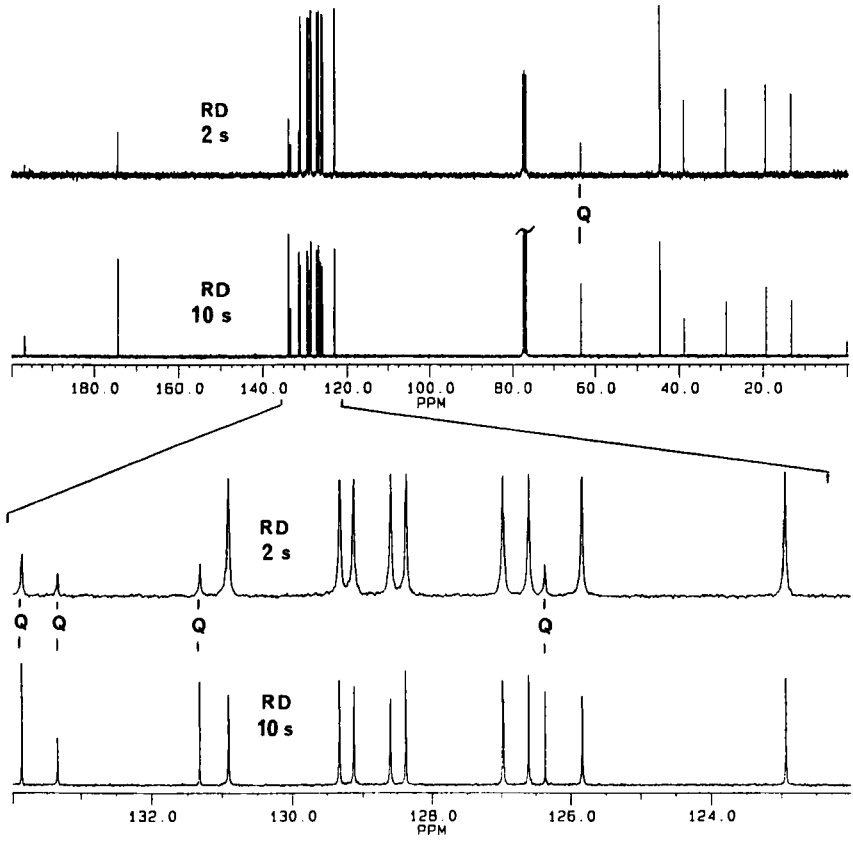



Figure 3. The 75 MHz $^{13}C$ NMR spectra of 2 in $CDCl_3$ (ambient temperatures) with composite pulse decoupling (CPD) for decoupling of protons. Intensity and chemical shift scales may differ for the different regions. Relaxation delays (RD, in sec) are as shown.

bridgehead phenyls, with a lesser effect for H-2,7, consistent with observed results (10c). The apparent anisotropic shieldings reported here for 2 are consistent with results for the phencyclone adduct of N-n-propylmaleimide (6).

Preliminary $^{13}C$ NMR data is presented here (in Figure 3 and Table 1b). The low intensity peak at lowest field, 196.75 ppm, is assigned to the single bridging ketone carbonyl and the higher

Table 1. NMR spectral data for 2 (in ppm).
a) Proton chemical shifts for adduct 2 and Reference Compounds.

| Nucleus | 2 | (Est'd J, Hz) | Phenanthrene (refs. 10a, 11) |
|---|---|---|---|
| H-1,8 | 7.155 | (8.25) | 8.12 |
| H-2,7 | 7.229 | | 7.82 |
| H-3,6 | 7.529 | (7.23) | 7.88 |
| H-4,5 | 8.639 | (8.44) | 8.93 |

| | 2 | | N-n-Butylmaleimide |
|---|---|---|---|
| CH | 4.409 | | 6.709 |
| $NCH_2$ (α) | 2.890 | (7.38) | 3.521 (t) |
| $CH_2$ (ß) | -0.223 | (6.78) | 1.570 (quintet) |
| $CH_2$ (γ) | 0.174 | | 1.310 (sextet) |
| $CH_3$ (δ) | 0.174 | | 0.927 (t) |
| H-2' | 8.350 | (7.76) | |
| H-3' | 7.724 | (7.14) | |
| H-4' | 7.529 | (7.23) | |
| H-5' | 7.428 | (7.51) | |
| H-6' | 7.217 | | |

| δ (ppm) | Tentative assignments |
|---|---|
| 196.75 | C=O (ketone) |
| 174.30 | 2 C=O (imide) |
| **Aryl $sp^2$** | |
| 133.87 | Q |
| 133.34 | Q |
| 131.32 | Q |
| 130.91 | |
| 129.32 | |
| 129.12 | |
| 128.59 | |
| 128.36 | |
| 126.97 | |
| 126.59 | |
| 126.36 | Q |
| 125.83 | |
| 122.93 | |
| **Alkyl $sp^3$** | |
| 63.35 | 2 Q, C-C=O |
| 44.45 | 2 CHC=O |
| 38.66 | $NCH_2$ |
| 28.65 | |
| 19.13 | |
| 13.18 | |

Notes: Chemical shifts for $^{13}C$ shown above obtained with relaxation delay of 2 sec; chemical shifts observed with other relaxation delays were typically within ca. 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 observed for these signals when using short relaxation delays. See Discussion.

intensity signal (at 174.30 ppm) is assigned to the two imide carbonyls. Among the six signals at higher field than the $CDCl_3$ signal, the peak at 63.35 ppm is attributed to the two unprotonated (4°, "Q") bridgehead carbons bearing the phenyls, based on their chemical shifts (by analogy with phencyclone adducts described earlier) and the relatively low peak intensity when a shorter relaxation delay is employed (e.g., RD = 2 sec versus 10 sec). The peak at 44.45 ppm is assigned to the two bridgehead methines alpha to the imide carbonyls (based on high signal intensity and analogy to previously reported adducts). We have not attempted to rigorously assign the four carbons of the butyl group. Most significant for this present study is the number of aryl carbon resonances. As shown (in Fig. 3, RD = 10 sec) thirteen distinct aryl signals are seen. This is fully consistent with slowly rotating bridgehead phenyls and SEL spectra, but is not compatible with rapidly rotating phenyls (in which case only eleven aryl peaks are predicted). Future studies will aim for carbon-13 NMR assignments via DEPT and 2D $^1H$-$^{13}C$ chemical shift correlation experiments (such as "XHCORR" or "HETCOR" and related sequences).

## CONCLUSIONS

We have synthesized the Diels-Alder adduct, 2, of N-n-butylmaleimide and phencyclone, and characterized the adduct by 1D and 2D $^1H$ and $^{13}C$ NMR studies at ambient temperatures in $CDCl_3$ solution. Full $^1H$ and preliminary tentative $^{13}C$ NMR spectral assignments have been made. The 300 MHz $^1H$ and 75 MHz $^{13}C$ spectral data are fully consistent with SEL spectra resulting from slow, hindered rotations of the unsubstituted bridgehead phenyls (on "the NMR timescales"). Several examples of magnetic anisotropy are invoked to account for: (a) deshielding of H-2', the ortho phenyl hydrogens that are proximal and roughly coplanar to the ketone carbonyl in the proposed favored conformation (with phenyls roughly perpendicular to the phenanthrene moiety); (b) shielding of the phenanthrene moiety protons (especially H-1,8 and 2,7) by the phenyls; and (c) shielding of the n-butyl group (especially the methylenes $\beta$ and $\gamma$ to the nitrogen) from the phenanthrene moiety. This is considered to support endo adduct stereochemistry. Anisotropic shielding magnitudes can be estimated by comparisons of the $^1H$ shifts in 2 with shifts in

selected reference compounds, i.e., phenanthrene and N-n-butylmaleimide. Future studies should provide additional understanding of hindered rotation and anisotropy in related systems.

ACKNOWLEDGMENTS

Partial support has been provided by the U.S. Education Department Minority Science Improvement Program (grant nos. G008641165 and 1-132553815-A1), National Science Foundation (grant nos. USE8851684 and USE9152822), Hewlett-Packard Corp., U.S. Department of Energy (ERLE), Hoffmann-La Roche Inc., Berlex Laboratories Inc. The Forty-Five Foundation, and the Professional Staff Congress - City University of New York Research Award Program (to R.R.)

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Received: May 17, 1996
Accepted: June 26, 1996