Tetrahedron. Vol. 30, pp. 719 to 726. Pergamon Press 1974. Printed in Great Britain

CONFORMATIONS OF HIGHLY HINDERED ARYL ETHERS—XVIII

NEIGHBORING-RING ANISOTROPY EFFECTS IN POLY(2,4-DINITROPHENOXY)BENZENES[1,2]

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(*Received in the USA* 6 *December* 1972; *Received in the UK for publication* 8 *November* 1973)

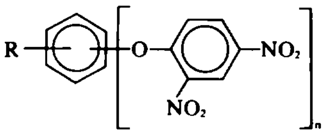
Abstract—A PMR study of ten poly-(2,4-dinitrophenoxy)benzenes and naphthalenes together with appropriate reference compounds, showed that (1) relatively long-range anisotropic effects are observed; (2) these are roughly additive when several benzene rings are present; (3) in the absence of steric effects there is no preference between *syn* and *anti* dispositions of substituting rings about the central ring; (4) concerted libration and concerted rotation occur freely even in highly substituted diaryl ethers; and (5) a twist conformation is preferred about the individual ether links.

INTRODUCTION

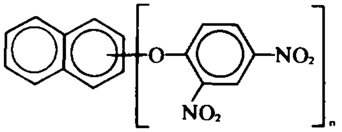
In continuation of our study on the preferred conformations of diaryl ethers,[2] it was of interest to investigate examples with several equivalent moieties present in the same molecule as an aid in clarifying further the question of conformational preferences in these and related compounds.[3-5] In previous NMR work[3,6-7] the chemical shift of substituents *ortho* to the ether linkage (H and F), was shown to constitute a sensitive probe in such studies. The 2,4-dinitrophenyl (DNP) moiety, with its characteristic steric and conjugative properties[8] and its easily detectable protons, was indicated for an investigation of more complex examples. The use of a convenient etherification reaction,[9] employing 1 - fluoro - 2, 4 - dinitrobenzene and appropriate phenols or amines, afforded compounds **1-16**, all of which incorporate one or more DNP residues.

In earlier work on this problem, we have obtained evidence from dipole moment determinations,[8, 10,11] NMR studies[3,7] and X-ray diffraction work[12] that 2,4-dinitrodiphenyl ethers preferentially adopt twist conformations (**1a** and **1c**) as the result of a balance between the conjugative tendency toward coplanarity and the steric hindrance by the *endo ortho* substituents toward achieving it. In these enantiomeric twist conformations the two rings are rotated out of coplanarity in opposite directions approximately 37° as estimated from the dipole moments of ten such ethers.[8]

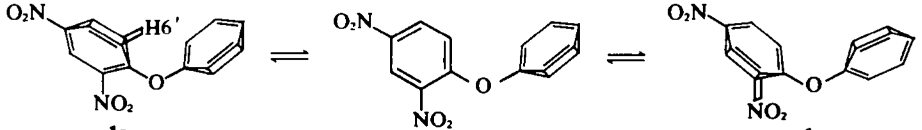
In solution, however, both *concerted libration*[3] and *concerted rotation*[13] occur readily. The first interconverts the twist conformers **1a** and **1c** *via* the skew conformation[6] **1b**. It will be noted that this



No.	n	Position(s)	R
1	1	—	H
2	2	1,2	H
3	2	1,3	H
4	2	1,4	H
5	3	1,2,3	H
6	3	1,3,5	H
7	1	1	3–NH–DNP
8	1	1	2–C_6H_5
9	1	1	2–CMe_3
10	0	—	NH–DNP

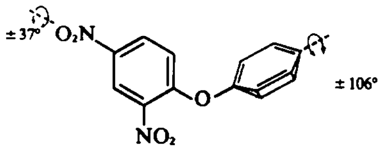


No.	n	Position(s)
11	1	2
12	1	1
13	2	1,3
14	2	1,4
15	2	2,7
16	2	2,3
17	2,4-Dinitroanisole	



1a **1b** **1c**

formulation is equivalent to an oscillation about the skew conformation **1b**



in which the "positioned" DNP ring rotates through a smaller angle than does the other ring. Nevertheless, the skew conformation must be of higher energy since both population-averaged (dipole moments) and time-averaged studies (NMR) indicate a preference for the twist conformation.

In addition, concerted rotation[13] about both ether linkages can lead, *via* high energy skew conformations to other twist conformations which, although less likely because they have a larger group (e.g. NO$_2$) in the *endo* location, have also been detected.[3,7]

The present work was undertaken since the presence in one molecule of several DNP residues could be expected to furnish further evidence in this regard: symmetry considerations, steric hindrance, and the mutual interaction of the magnetic anisotropies of several aromatic systems in difinite stereochemical relation, would provide further data in the analysis of the conformational preference of diaryl ethers.

RESULTS*

PMR assignments

The apparent chemical shifts of the compounds studied are gathered in Table 1. These were assigned on the basis of first-order analyses, although the spectra are not strictly first-order in all cases (ave. $\Delta\nu/J = 7{\cdot}7$ for H5 and H6 of the dinitro rings). Internal comparison of a large number of related compounds further minimizes the importance of this approximation. The protons on the central ring gave complex multiplets not resolved at this field strength; in two cases (3 and 7) it was possible to determine the chemical shifts of these protons also by analogy with the patterns of similarly substituted benzenes. Since these are tentative and approximate (no calculations were performed) they were not used for conformational assignments. The signal assignments for the pertinent protons were straightforward in most cases since chemically equivalent substituents (e.g. in **2**, **3**, **4** and **6**) give a single set of signals. Three exceptions were **5**, **7** and **13** in which they were assigned as follows:

(a) *Compound* **5** (Fig 1). The presence of two unequivalent substituents, i.e. the outer DNP moieties at 1 and 3, and the inner one at 2, results in two sets of signals. Starting at low fields, the first two pairs of peaks can be assigned to the protons at position 3 because of their location between two nitro groups and because of their *meta* splitting pattern. The ratio of their integrals (2:1) allows them to be assigned respectively to H3′ and H3‴ on the two equivalent outer rings and to H3″ on the inner dinitroring. (Peaks 3 to 6 do not belong to one set of protons because peaks 3 and 4 separate slightly from 5 to 6 at lower concentrations.) The next six peaks (between 8·6 and 8·3 ppm) correspond to the superposition of the signals from 5′, 5″ and 5‴, as shown by their position (*ortho* to a nitro-group) and by their *ortho*, *meta* splitting patterns. At higher field is found a three-proton multiplet which was assigned to the nearly equivalent protons (4, 5 and 6) of the central ring. Finally, at highest fields are found the two doublets (*J ca* 10 Hz) for the positioned protons. The higher-field doublet was as-

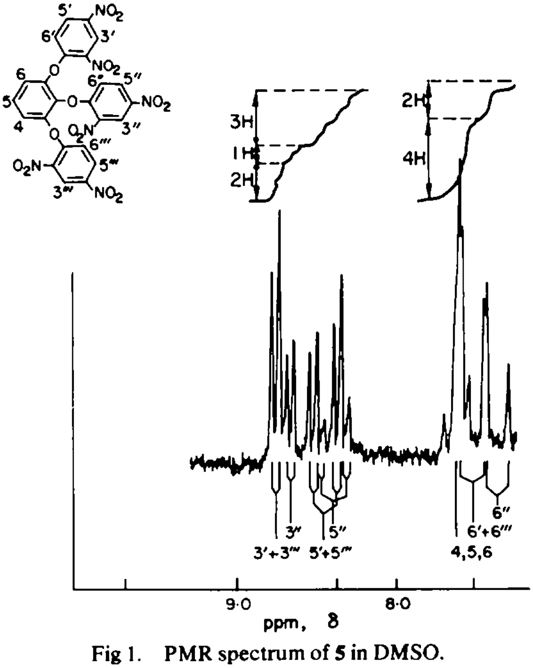


Fig 1. PMR spectrum of **5** in DMSO.

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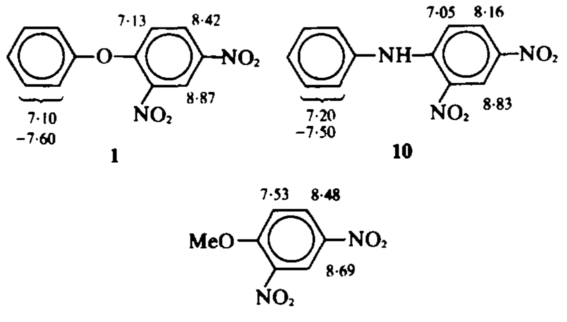
*For the sake of simplicity and consistency throughout this paper, the poly-DNP benzenes are numbered such that the central ring is unprimed, while its substituting rings are primed, double-primed and triple-primed in the order of their position on the central ring.

signed to H6″ on the inner dinitro-ring because its high-field peak has a height equal to that of the lower-field peak of proton 3″, while the lower-field doublet was assigned to protons 6′ and 6‴ on the two equivalent outer dinitro-rings. Peak integration, repeated several times, confirmed the assignments.

(b) *Compound* **7**. The DNP ring protons in **7** were assigned by comparison to **1** and **10**, in which the NH–DNP ring protons appear at higher fields than the corresponding ones on the O–DNP ring.

(c) *Compound* **13**. The protons of the DNP moieties of this ether were assigned by comparison with **11** and **12**, the protons on the αO–DNP moiety appearing always at higher fields. Reversing these assignments gave shifts inconsistent with the overall trend of the results.

Chemical shift differences To facilitate a comparison of the chemical shifts in these compounds, the results have been gathered in Fig 3, in which the shift differences are given relative to the appropriate reference compound (**1** or **10**) whose shifts are shown in Fig 2. Those shown were obtained in DMSO in which all compounds were soluble; simi-



1 **10** **17**

Fig. 2. Structures and PMR chemical shifts (ppm in DMSO) of the reference compounds **1**, **10** and **17**.

Table 1. PMR chemical shifts of (2,4-dinitrophenoxy)benzenes and naphthalenes.

No.	Solvent[a]	Non-nitro ring protons	Dinitro ring protons[b] 6′	5′	3′	6″	5″	3″
1	D	2 − 6 = 7·10 − 7·60[c]	7·13	8·42	8·87	—	—	—
	C	2 − 6 = 7·00 − 7·83[c]	7·05	8·33	8·83	—	—	—
2	D	3 − 6 = 7·56	7·18[d]	8·41	8·77	—	—	—
	C	3 − 6 = 7·66	7·28	8·53	8·84	—	—	—
3	D	2 = 7·27, 4 + 6 = 7·22, 5 = 7·63	7·35[d]	8·45	8·86	—	—	—
4	D[e]	2 − 6 = 7·42	7·32[d]	8·47	8·91	—	—	—
5	D[f]	4 − 6 = 7·66	7·56[d]	8·49	8·83	7·41	8·39	8·73
6	D[e]	2 + 4 + 6 = 7·31	7·58	8·53	8·91	—	—	—
	A	2 + 4 + 6 = 6·83	7·25	8·13	8·43	—	—	—
7	D[g]	2 = 7·25, 4 + 6 ~ 7·48, 5 ~ 7·33	7·33	8·48	8·84	7·26	8·21	8·84
8	D	3 − 6 + 2″ − 6″ = 7·17 − 7·67[c]	6·95	8·27	8·71	—	—	—
	C	3 − 6 + 2″ − 6″ = 7·08 − 7·75[c]	6·73	8·10	8·66	—	—	—
9	D	3 − 6 = 7·08 − 7·50[c]	7·10	8·43	8·90	—	—	—
	C	3 − 6 = 6·75 − 7·75[c]	7·07	8·37	8·92	—	—	—
10	D[g]	2 − 6 = 7·20 − 7·50[c]	7·05	8·16	8·83	—	—	—
	C[g]	2 − 6 = 7·33 − 7·66[c]	7·20	8·21	9·21	—	—	—
11	D	1 + 3 − 8 = 7·41 − 8·17[c]	7·23	8·41	8·90	—	—	—
12	D	2 − 8 = 7·25 − 8·08[c]	6·97	8·33	8·91	—	—	—
	C	2 − 8 = 7·15 − 8·11[c]	6·88	8·23	8·88	—	—	—
13	D	2 + 4 − 8 = 7·41 − 8·17[c]	7·28[h]	8·38	8·86	7·41	8·43	8·91
14	D	2,3,5,6,7,8 = 7·41 − 8·17[c]	7·20[d]	8·33	8·91	—	—	—
15	D	1,3,4,5,6,8 = 7·41 − 8·25[c]	7·30[d]	8·43	8·90	—	—	—
16	D	2 + 4 − 8 = 7·41 − 8·17[c]	7·35[d]	8·41	8·83	—	—	—
17	D	CH_3O = —	7·53	8·48	8·69	—	—	—
	C	CH_3O = 4·11	7·25	8·46	8·74	—	—	—

[a] D = DMSO, C = $CDCl_3$, A = CH_3COCH_3; the chemical shifts in DMSO are given relative to internal TMS, but accurately measured from the DMSO signal at $\delta = 2{\cdot}50$.

[b] Coupling constants: *ortho*, 9–10 Hz; *meta*, 3 Hz. Correct integrations were obtained in all cases.

[c] Unresolved multiplet spanning the range indicated.

[d] Signals from the protons of two equivalent rings.

[e] Saturated solution, *ca* 25 mg/ml.

[f] See Fig 1.

[g] NH-proton appears at $\delta = 10{\cdot}05$.

[h] Signals from protons on O–DNP ring attached at position 1.

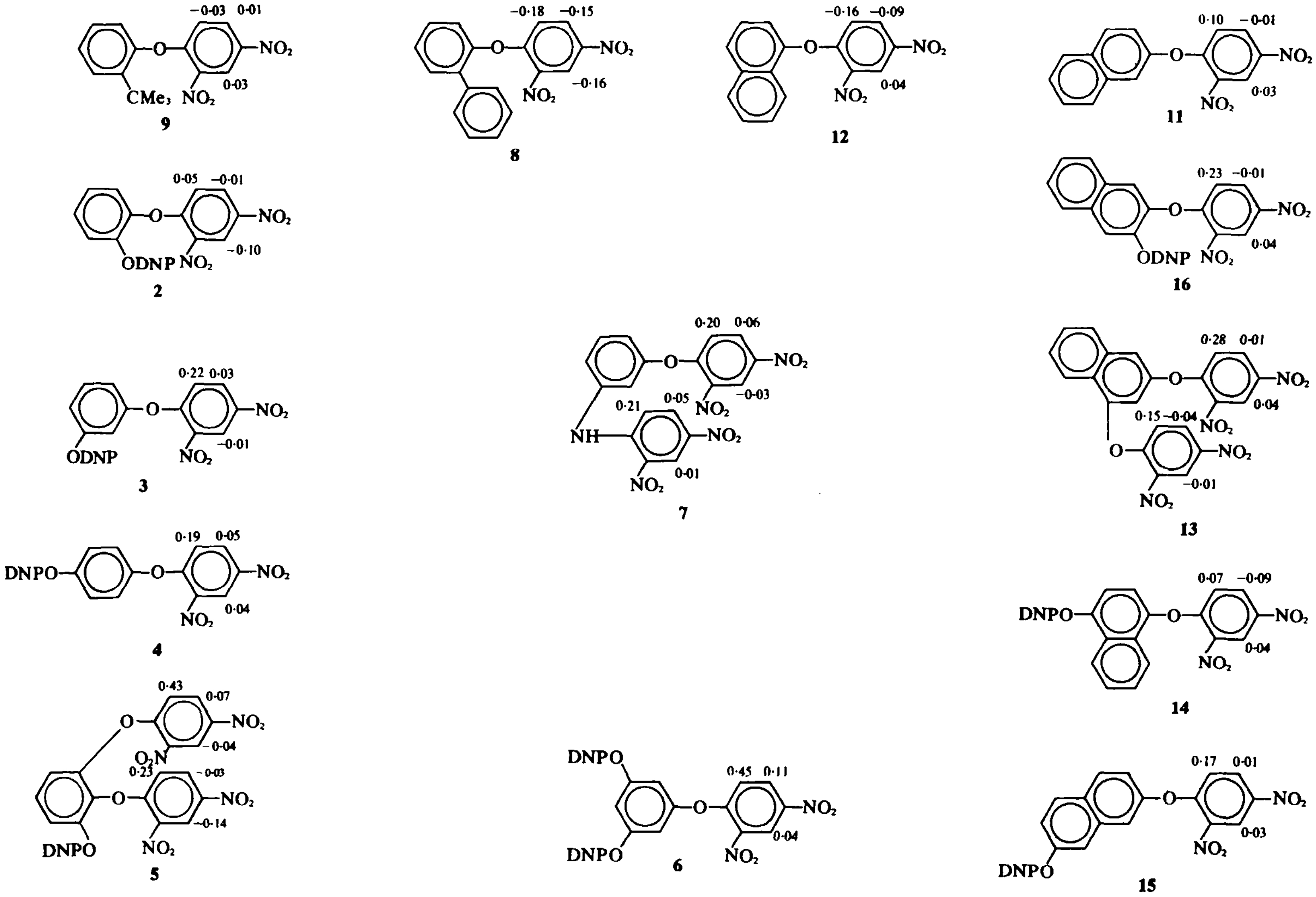


Fig 3. Chemical shift differences (ppm in DMSO) relative to **1** or **10**; DNP indicates the presence of another equivalent residue with identical chemical shifts to those shown.

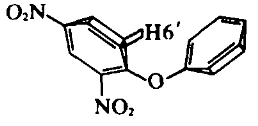
lar shifts were also obtained in cases where comparison was possible in $CDCl_3$ and acetone (Table 1).

Comparison with calculated shifts. In Table 2 are compared the shifts calculated (Experimental) for the magnetic anisotropy effect of neighboring aromatic rings on the positioned protons with those actually observed in one or more compounds bearing the corresponding interacting moieties.

DISCUSSION

A. *Conformation of the reference ether* 1[*]

A comparison of the chemical shifts observed for **1** with those obtained under identical conditions for the corresponding anisole[14] **17** shows that H6′ in the phenyl ether experiences a net shielding of −0·40 ppm (in DMSO), attributed to the magnetic anisotropy of the benzene ring.[6,7] This shielding is significantly smaller than that calculated for the skew conformation (−1·0) and corresponds to that calculated for the twist conformation (**1a**). On this basis, and other available evidence discussed above, it would seem that **1** adopts preferentially the twist conformation **1a**.



1a

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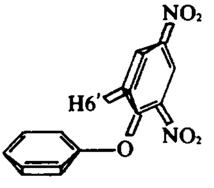

1a

In the discussion which follows, the anisotropic effect of the non-nitro ring has been subtracted out by comparing all observed shifts to those of **1** (Fig 3), which permits the detection of the anisotropic effects due to other aromatic substituents.

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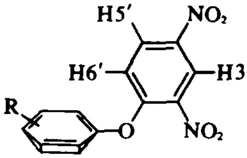
[*] In view of the numerous necessary assumptions (compound geometry), approximations (ring current model, possible concentration dependency) and lack of information (specific solvent and substituent interactions), the estimates of shifts and shieldings, although stated quantitatively, should be taken to give no more than a qualitative picture of conformational preference.

Table 2. Comparison of calculated and observed shieldings for DNP ethers[a]



R		Calculated shifts[b]			Compound	Observed shifts		
		H6′	H5′	H3′		H6′	H5′	H3′
$2\text{-}C_6H_5$	$\theta = 0°$	0·04	0	0·04	**8**	−0·18	−0·15	−0·16
	$\theta = 45°$	0·06	−0·06	−0·20				
[*c*]-Benzo		0·24	0	0	**11**	0·10	−0·01	0·03
[*b*]-Benzo		−0·07	−0·11	0	**12**	−0·16	−0·09	0·04
2-*O*–*DNP*	*syn*	0·42	0·13	−0·28	**2**	0·05	−0·01	−0·10
	anti	0·13	0	−0·03				
					5	0·43[c]	0·07	−0·04
						0·28[c]	−0·03	−0·14
					16	0·23[c]	−0·01	0·04
3-*O*–*DNP*	*syn*	0·20	0	0	**3**	0·22	0·03	−0·01
	anti	0	0	0				
					7	0·20[d]	0·06	−0·03
						0·21[e]	0·05	0·01
					13	0·28[c]	0·01	0·04
						0·15	−0·04	−0·01
					6	0·45[c]	0·11	0·04
4-*O*–*DNP*	*syn*	0·13	0	0	**4**	0·19	0·05	0·04
	anti	0	0	0				
					14	0·07[c]	−0·09	0·04

[a] Shieldings are negative, deshieldings are positive

[b] Shifts calculated for the skew conformation; see Discussion.

[c] Result of two independent aromatic systems.

[d] Of the O–DNP ring protons.

[e] Of the NH–DNP ring protons.

B. *Central ring protons*

The chemical shifts (Table 1) of the protons on the central (non-dinitro) ring in this series vary over the normal range for benzene ($\delta = 7{\cdot}1$–$7{\cdot}7$) and naphthalene ($\delta = 7{\cdot}2$–$8{\cdot}3$) aromatic protons, and show no special relationship to the number or position of the DNP substituents present. In view of this it is unlikely that inductive effects are being transmitted between two such substituting rings through the central ring or that their presence sufficiently alters the π-cloud density on the central ring so as to affect the observed shifts of the positioned protons.

C. *The positioned ortho proton*

(1) *Effect of steric hindrance.* A comparison of compound **9** with **1** (Fig 3) shows that a bulky substituent on the central ring has negligible conformational effects. This is in accord with earlier findings[8] and reasonable since **9** can adopt a twist conformation in which there is no steric interference between the *ortho* substituents. Similar considerations apply to all the other compounds in this series.

(2) *Effect of fixed neighboring aromatic rings.** The naphthyl ethers **12** and **11**, which can be considered as [*b*]- and [*c*]-benzo derivatives of **1**, show strong effects due to the annellated ring. Thus in the α-naphthyl ether **12** the positioned *ortho* proton H6′ is shielded by $-0{\cdot}16$ ppm, whereas in the β-naphthyl ether it shows a deshielding of $+0{\cdot}10$ ppm. These shifts are qualitatively, but not quantitatively in agreement with those calculated for the skew conformation (Table 2).

Entirely similar results were found for the biphenyl derivative **8** in which the 2-phenyl substituent clearly produces a net shielding. The shielding calculated for it in the skew conformation (Table 2) was smaller for all twist angles θ of the bond connecting this substituent to the central ring, thus indicating that also in this ether steric interference between the nitro group and the additional phenyl ring leads to adoption of the twist conformation.

(3) *Effect of mobile neighboring aromatic groups.* A cursory inspection of the shift differences found for the compounds shown in the lower part of Fig 3 shows that, with a few minor exceptions, all the protons on the DNP moieties are *deshielded.*

(a) 1,3-*Bis-DNP substitution.* Beginning with ether **3**, it is readily seen that the two DNP rings exert mutual deshielding effects on each others protons, most noticeably on the positioned protons H6′ and H6″. Since in this ether there is no steric hindrance present, two different overall arrangements are possible, *syn* and *anti*, with equal statistical distribution as shown in Fig 4. Measurements on models (Table 2), using skew conformations as approximations of the true twist arrangements, showed that no deshielding is to be expected for the *anti* conformer, whereas a deshielding of 0·20 ppm is predicted for the *syn* conformer. In view of this, the observed deshielding of 0·22 ppm is best rationalized by attributing it entirely to the *syn* conformer whose substituting rings when in the twist arrangement show a true mutual deshielding of about 0·40 ppm, double that observed.

Three further ethers with the same 1,3-substitution pattern (**6**, **7** and **13**) corroborate this interpretation: In ether **6** each positioned proton is subjected to the effect of *two* other DNP rings, and in effect the observed difference is twice that in **3** (0·45 ppm). In **7**, the same difference is seen as in **3**, showing that an NH–DNP substituent behaves similarly to an O–DNP substituent, as would be predicted. Finally in **13**, the positioned protons show the anisotropic effects of both the other DNP moiety and of the annelated ring; the observed position of H6′ (on 1-DNP) is shielded relative to **3** whereas H6″ (on 3-DNP) is deshielded relative to **3** in accord with the results described earlier for **11** and **12**.

(b) 1,4-*Bis-DNP substitution.* A comparison of **4** with **1** shows a similar deshielding, slightly reduced as a result of the (slightly) larger separation present here as compared to the previous cases. In **14** the observed deshielding of 0·07 ppm is the resultant of a the mutual deshielding (due to *peri* interactions as in **12**), offset by the shielding due to the annelated ring.

(c) 2,7-*Bis-DNP substitution.* In **15** a slightly reduced deshielding is observed on account of the larger separation, but surprisingly a strong mutual interaction is still present.

(d) 1,2-*Bis-DNP substitution.* In ether **2** the observed deshielding is slightly less than that calculated of 0·13 ppm, possibly a result of repulsive dipole–dipole interaction[11] between the two *ortho*-nitro groups in the *anti* disposition which would lead to a less propitious interaction of the two substituting rings. In compound **16** a net deshielding of 0·23 ppm is observed, which is the result of a moderate mutual deshielding of the *ortho* DNP moieties plus the deshielding due to the annelated ring, as was seen in **11**.

Finally in the last and possibly most interesting example of the series, the triply substituted benzene **5**, approximate additivity of the mutual deshieldings is again observed. Thus the positioned protons on the two outer rings (Fig 1, H6′ and H6‴ and Fig 4) show a deshielding which is the sum of the effects experienced due to each other (0·22) plus that from the middle ring, now positioned more nearly in the skew conformation due to the presence of two symmetrically disposed nitro groups. The observed shift for the positioned proton of the

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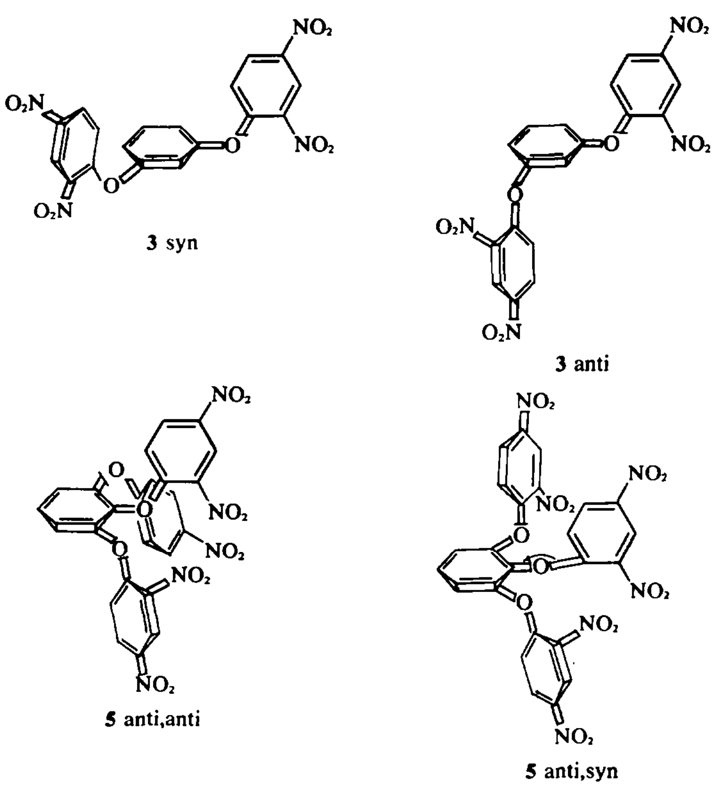
*In the absence of contrary information, it is here assumed that the ring currents of two or more benzene rings produce equal magnetic anisotropic effects independently of each other.



3 syn

3 anti

5 anti,anti

5 anti,syn

Fig 4. Conformations of ethers 3 and 5. For simplicity skew arrangements are shown as an approximation of the true twist arrangements.

inner ring (H6″) shows a larger deshielding (0·28) than that predicted from two *ortho* DNP interactions (0·10). This, however, is easily ascribed to the fact that on a statistical basis concerted rotation would lead to an appreciable population of the *anti, syn* conformer (Fig 4). Two *syn* disposed DNP moieties were calculated to exert mutual deshieldings of 0·42 ppm, more than enough to make up the observed discrepancy.

D. *The positioned* meta *and* para *protons*

Examination of the results presented in Tables 1 and 2 shows that the other positional protons also experience shifts due to the presence of other aromatic moieties. Although in general they reflect the trends seen for the ortho positioned proton, the smallness of their shifts does not warrant detailed discussion.

EXPERIMENTAL

General. M.ps were obtained with a Kofler hot-stage and are given uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

PMR spectra were obtained on a Varian A-60 spectrometer. Some of the ethers studied were not sufficiently soluble in $CDCl_3$, whereas all of them were soluble in DMSO to the extent necessary for unequivocal signal assignment and for comparison among themselves, as well as with some related cyclic ethers.[15] Since slight concentration shifts were observed for certain signals, all spectra were recorded at 50·0 mg/ml. Chemical shifts were accurately measured from the DMSO peak ($\delta = 2{\cdot}50$) but are given relative to TMS.

Compounds used. Most of the compounds used were available from earlier work.[9,14] In view of discrepancies[9] in the reported m.ps of **5** and **6**, these were prepared also by a different method (Hems–Meltzer synthesis)[7] and analyzed. For **5** a m.p. of 165–172° was found and for **6** it was 190–195°. (Found for **5**, C = 45·90, H = 1·84, N = 13·81, and for **6**, C = 46·34, H = 2·23 and N = 13·43, for both ($C_{24}H_{12}O_{15}N_6$), Calcd C = 46·15, H = 1·93, N = 13·46%). Compound **10** was prepared as usual[9] and gave material whose properties agreed with those reported.[16] Compounds **14** and **16** were prepared as described below.

1, *4-Bis-(2, 4-dinitrophenoxy)naphthalene* (**14**). On account of the facile oxidation of the 1, 4-naphthalenediol, the usual method[9] failed. This compound could be obtained as follows. The diol (1·6 g, 0·01 moles) dissolved in DMF (100 ml) was treated with 1-fluoro-2,4-dinitrobenzene (3·72 g, 0·02 moles) and triethylamine (2·2 g, 0·022 moles) and the mixture was refluxed for 4 h under N_2. After cooling, 200 ml water was added and the mixture extracted with 3 portions of $CHCl_3$ 50 ml each. The combined extracts were washed twice with 100 ml of 2·5 Na_2CO_3 aq and twice with 100 ml of water. After drying, and charcoal treatment, the soln was taken to dryness.

The resulting material was crystallized from 25 ml acetone and 25 ml CCl_4. There was obtained 700 mg (14%) of a yellow powder, m.p. 243–244°. (Found: C = 53·85, H = 2·37 and N = 11·21. Calcd for $C_{22}H_{12}N_4O_{10}$: C = 53·67, H = 2·46, N = 11·38%).

2, 3-*Bis*(2, *4-dinitrophenoxy*)*naphthalene* (**16**). Prepared in the usual way.[9] There was obtained a 72% yield of slightly yellow crystals with m.p. 142–143°. (Found: C = 53·24, H = 2·33, and N = 11·72. Calcd for $C_{22}H_{12}N_4O_{10}$: C = 53·67, H = 2·46, N = 11·38%).

Calculated shieldings. These were obtained analytically or by measuring accurately on framework molecular models (Dreiding or Fieser) the distances (in cylindrical coordinates) separating a given proton from the center of a neighboring benzene ring. An oxygen valency angle of 120° for the ether bridge and symmetrical hexagons with benzene dimensions were assumed, based on what was found in another DNP ether by X-ray crystallography.[12] After conversion to ring-radius dimensions (ρ and z values) the appropriate shielding or deshielding was obtained from tables.[17] Use of the recently revised tables[18] did not alter the results significantly.

Since for most of the compounds discussed, both of the two most probable twist conformations are equally probable, the calculated shieldings were obtained by considering skew arrangements which are good approximations in such cases for the true situation.

Acknowledgement—It is a pleasure to acknowledge here the able technical assistance of Q.F.B. Arturo Ramírez M.

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