Journal of Molecular Structure
Elsevier Publishing Company, Amsterdam. Printed in the Netherlands

CONFORMATIONS OF HIGHLY HINDERED ARYL ETHERS

II. DIPOLE MOMENTS OF 2,4-DINITROPHENYL PHENYL ETHERS*

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(Received January 13th, 1970; in revised form April 22nd, 1970)

ABSTRACT

The dipole moments of nine 2,4-dinitrophenyl R′-phenyl ethers [R′ = H, 2′-Me, 2′-I, 2′-F, 2′,4′-Br_2, 2′,4′-$(NO_2)_2$, 2′,6′-Me_2, 2′,6′-$(iPr)_2$ and 2′,4′,6′-Br_3] have been measured and compared with calculated values for a variety of conformations. Agreement was found for three possible conformations and for concerted rotation of the phenyl rings about the ether bond. In two of the conformations the phenyl rings are twisted 37° from coplanarity in opposite directions. The third conformation is one in which the two rings are perpendicular to one another, the 2,4-dinitrophenyl ring being in the plane of the ether bond with the 2-nitro group *distal* to the R′-ring. It is concluded that at 25° concerted rotation occurs with possible increased populations of the three conformations. Several previously proposed conformations are ruled out by these measurements.

INTRODUCTION

The problem of preferred conformations in diaryl ethers has been studied for over forty years without having been solved satisfactorily. A variety of valency angles and conformations have been proposed on the basis of chemical reactivity[1,2], yields in ring closure reactions[3], UV[4-6], IR[5,7,8] and Raman spectroscopy[7], X-ray diffraction[9], electron diffraction[10,11], PMR[12-17], EPR[18], molecular orbital calculations[19], calorimetry[20], and various polarization methods such as dipole moments[21-28], dielectric relaxation[29-35], and molar Kerr constants[36]. However, it has not been possible to decide whether there are any preferred conformations, and if so, which they are, and whether they depend on the pattern of substitution in the *ortho* positions.

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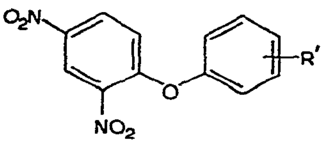
* Portions of this work were presented at the Fifth Mexican Congress of Pure and Applied Chemistry held in Mérida, Yucatán, April 9–11, 1970. For Part I, see ref. 38.

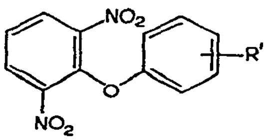
It seemed to us that a study of compounds selected on the basis of bulky substituents with large group moments and using PMR in conjunction with dipole moment measurements might be of use in the solution of this problem. Although highly hindered diphenyl ethers have been prepared (e.g. 2,6-dinitro-2′,6′-dichlorodiphenyl ethers[5]), these have been examined only by UV and IR[5]. Conversely, dipole moment studies have been carried out only on 2,2′-disubstituted analogs[25,28]. On the other hand PMR has been used to study tri-*ortho*-substituted analogs[14,15,17] of limited types and a few tetra-*ortho*-substituted examples[14,15].

We chose as a substituent the nitro group, not only because of its bulk and large group moment, but also because the highly hindered compounds required can be synthesized easily with it and because it can be converted to an iodo group which is of interest in the study of the thyroid hormones[37]. The other substituents were chosen so as to provide various combinations of size (H and F vs. Me, iPr, Br, I and naphthyl) and group moments (H, Me, iPr and naphthyl vs. F, Br and I).

The compounds studied were of three types: 2,4-dinitrophenyl (A), 2,6-dinitrophenyl (B) and 2,4-dinitronaphthyl (C) phenyl ethers, substituted in the non-nitro ring at different positions, mainly 2′, with the aforementioned substituents.



(A)



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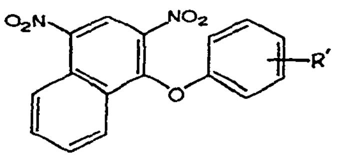


(C)

The dipole moment results of type A are presented here, while those for B and C will be presented in a separate communication. The PMR studies of all of these compounds will be presented elsewhere. The group moments of the dinitro moieties not available in the literature were determined as described in Part I[38] of this series.

EXPERIMENTAL

Materials

The 2,4-dinitrophenyl phenyl ethers (Table 1) were synthesized according to Bost and Nicholson[39] from 2,4-dinitrochlorobenzene or by Reinheimer's modification[40] using 2,4-dinitrofluorobenzene. 2,4,2′,4′-Tetranitrodiphenyl ether (II-6) could not be obtained by these methods nor by the addition of KF as suggested by Vorozhtsov and Yakobson[41]. It was prepared in good yield by nitration of diphenyl ether according to Matsumura[42]. The samples used for the dipole moment

TABLE 1

SYNTHESIS AND PROPERTIES OF 2,4-DINITROPHENYL R′-PHENYL ETHERS

Compound No.	*R′*	*Method of preparation*	*Yield (%)*	*m.p. (°C)*	*Reference or analysis*		*% C*	*% H*	*% N*	*% other*
II-1	H	Ref. 40	69	71–72						
				69 (lit.)	Refs. 5, 39, 47					
II-2	2′-F	Ref. 40	41	82–83	Found		52.10	2.03	10.17	F, 6.84
				—	$C_{12}H_7N_2O_5F$	req.	51.81	2.58	10.07	F, 6.83
II-3	2′-Me	Ref. 39	50	91–92						
				90 (lit.)	Ref. 39					
II-4	2′-I	Ref. 40	46	92–93						
				95 (lit.)	Refs. 39, 40					
II-5	2′,4′-Br_2	Ref. 40	89	129–131						
				135 (lit.)	Refs. 39, 40					
II-6	2′,4′-$(NO_2)_2$	Ref. 42	44	195–197						
				195–197 (lit.)	Ref. 42					
II-7	2′,6′-Me_2	Ref. 40	66	110–112	Found		58.25	4.09	9.63	
				—	$C_{14}H_{12}N_2O_5$	req.	58.33	4.20	9.72	
II-8	2′,6′-$(iPr)_2$	Ref. 40	33	82–84[a]	Found		62.67	5.77	8.09	
				—	$C_{18}H_{20}N_2O_5$	req.	62.78	5.85	8.13	
II-9	2′,4′,6′-Br_3	Ref. 40	77	114–116[b]	Found		29.13	1.19	5.55	Br, 48.25
				—	$C_{12}H_5N_2O_5Br_3$	req.	29.00	1.01	5.64	Br, 48.25

[a] This compound is reported in ref. 17 without m.p. or analysis.

[b] Although our m.p. for this compound differs from that in the literature (135[39], 135[40], 131–132[48], 130.5[49]) its structure was assured by the elemental analysis which showed the presence of three bromine atoms and its PMR spectrum, which showed a sharp singlet at 7.83 p.p.m.[50].

measurements were purified to at least 99.95 % by passage through alumina columns and recrystallization from ethanol. Many of these compounds, especially those containing iodine are light-sensitive.

Methods

The apparatus, the methods used, the determination of purity of the compounds and the means of calculating the dipole moments (DM) were described in Part I[38].

RESULTS AND DISCUSSION

The data and results of the dipole moment determinations are given in Tables 2 and 3, while Table 4 shows the measured dipole moments of these compounds and those calculated for different conformations which have been proposed for diphenyl ethers.

TABLE 2

DIPOLE MOMENT MEASUREMENTS: WEIGHT FRACTION VERSUS DIELECTRIC CONSTANT AND SPECIFIC VOLUME

$10^3\omega_2$	ε_{12}	v_{12}	$10^3\omega_2$	ε_{12}	v_{12}	$10^3\omega_2$	ε_{12}	v_{12}
2,4-Dinitrodiphenyl ether (II-1)			*2,4-Dinitro-2′-fluorodiphenyl ether (II-2)*			*2,4-Dinitro-2′-methyldiphenyl ether (II-3)*		
0.000	2.281	1.14465	0.000	2.283	1.14511	0.000	2.281	1.14599
0.499	2.285	1.14446	0.479	2.290	1.14462	0.477	2.286	1.14500
0.923	2.291	1.14426	0.921	2.294	1.14454	0.902	2.289	1.14450
1.587	2.298	1.14398	1.585	2.303	1.14419	1.580	2.298	1.14428
2.044	2.305	—	2.034	2.309	1.14397	2.027	2.303	1.14399
2.474	2.310	—	2.466	2.317	1.14388	2.514	2.308	1.14381
2,4-Dinitro-2′-iododiphenyl ether (II-4)			*2,4-Dinitro-2′,4′-dibromodiphenyl ether (II-5)*			*2,4,2′,4′-Tetranitrodiphenyl ether (II-6)*		
0.000	2.281	1.14485	0.000	2.274	1.14474	0.000	2.273	1.14472
0.467	2.286	1.14468	0.359	2.275	1.14454	0.458	2.275	1.14439
0.924	2.290	1.14452	0.684	2.278	1.14426	0.943	2.278	1.14423
1.588	2.294	1.14403	1.148	2.279	1.14409	1.590	2.282	1.14375
2.060	2.300	1.14363	1.500	2.281	1.14364	2.092	2.286	1.14343
2.474	2.304	1.14343	1.841	2.282	1.14358	2.500	2.288	1.14334
—	—	—	2.159	2.285	1.14336	—	—	—
—	—	—	2.526	2.286	1.14276	—	—	—
2,4-Dinitro-2′,6′-dimethyldiphenyl ether (II-7)			*2,4-Dinitro-2′,6′-diisopropyldiphenyl ether (II-8)*			*2,4-Dinitro-2′,4′,6′-tribromodiphenyl ether (II-9)*		
0.000	2.272	1.14503	0.000	2.274	1.14507	0.000	2.273	1.14480
0.467	2.280	1.14490	0.320	2.278	1.14489	0.345	2.275	1.14460
0.927	2.287	1.14465	0.679	2.282	1.14471	0.680	2.276	1.14436
1.575	2.291	1.14445	1.130	2.283	1.14479	1.148	2.278	1.14407
2.038	2.293	1.14425	1.484	2.286	1.14457	1.491	2.280	1.14385
2.509	2.299	1.14403	1.814	2.290	1.14433	1.840	2.282	1.14360
—	—	—	2.165	2.292	1.14435	2.171	2.284	1.14335
—	—	—	2.518	2.294	1.14413	2.529	2.286	1.14316

TABLE 3

DIPOLE MOMENT RESULTS FOR 2,4-DINITROPHENYL R′-PHENYL ETHERS

Compound No.	*R′*	ε_1	d_1	α*	β*	$P_{2\infty}$	M_R	$\mu(D)$
II-1	H	2.280	0.87363	40.05	1.071	642.89	63.47	5.32±0.12
II-2	2′-F	2.281	0.87337	47.66	1.322	752.46	63.24	5.80±0.11
II-3	2′-Me	2.279	0.87308	38.57	1.787	604.41	68.11	5.12±0.04
II-4	2′-I	2.280	0.87343	44.38	2.241	713.33	76.92	5.58±0.03
II-5	2′,4′-Br_2	2.274	0.87357	26.75	2.685	453.52	78.90	4.28±0.12
II-6	2′,4′-$(NO_2)_2$	2.272	0.87361	28.46	1.938	478.52	74.82	4.44±0.06
II-7	2′,6′-Me_2	2.274	0.87333	36.19	1.118	595.91	72.76	5.06±0.27
II-8	2′,6′-$(iPr)_2$	2.276	0.87336	31.74	1.136	548.84	91.36	4.73±0.40
II-9	2′,4′,6′-Br_3	2.273	0.87351	32.48	3.201	549.02	89.61	4.74±0.09

* α and β are the slopes of dielectric constant and density respectively vs. mole fraction.

ABLE 4

OMPARISON OF MEASURED AND CALCULATED DIPOLE MOMENTS FOR 2,4-DINITROPHENYL R′-PHENYL ETHERS

	II-1	*II-2*	*II-3*	*II-4*	*II-5*	*II-6*	*II-7*	*II-8*	*II-9*	*Av. abs. diff. %*
′ =	*H*	*2′-F*	*2′-Me*	*2′-I*	*2′,4′-Br_2*	*2′,4′-$(NO_2)_2$*	*2′,6′-Me_2*	*2′,6′-$(iPr)_2$*	*2′,4′,6′-Br_3*	
Ieasured DM (D)	5.32	5.80	5.12	5.58	4.28	4.44	5.06	4.73	4.74	
oncerted rotation $\theta = \theta' + 90°$	4.65 −13*	5.15 −11	4.59 −10	5.07 −9	4.14 −2	5.28 +19	4.08 −19	4.08 −14	4.65 −1	12
kew (1); 2-NO_2*distal* $\theta = 0°$ $\theta' = 90°$	5.57 +5	6.42 +11	5.40 +5	6.31 +13	4.97 +16	4.97 +12	5.16 +2	5.16 +9	5.57 +19	10
wisted (1) $\theta = 37°$ $\theta' = 37°$	5.07 −5	5.60 −3	4.92 −4	5.52 −1	4.21 −1	3.75 −16	4.69 −7	4.69 −1	5.18 +10	6
wisted (2) $\theta = 37°$ $\theta' = 217°$	5.07 −5	6.14 +6	4.90 −4	6.02 +8	4.95 +16	5.35 +20	4.69 −7	4.69 −1	5.18 +10	9
lanar (1) *cis* $\theta = 0°$ $\theta' = 0°$	5.57 +5	6.46 +11	5.37 +5	6.36 +14	5.03 +18	4.91 +11	5.16 +2	5.16 +9	5.57 +19	9
lanar (2) *trans* $\theta = 0°$ $\theta' = 180°$	5.57 +5	6.40 +10	5.40 +5	6.30 +13	4.95 +16	3.95 −11	5.16 +2	5.16 +9	5.57 +19	10
lanar (3) $\theta = 180°$ $\theta' = 180°$	3.93 −26	5.03 −13	3.67 −28	4.91 −12	5.44 +28	8.80 +98	4.07 −20	4.07 −14	3.93 −16	29
lanar (4) $\theta = 180°$ $\theta' = 0°$	3.93 −26	2.56 −56	4.33 −15	2.67 −52	3.11 −27	4.91 +11	4.07 −20	4.07 −14	3.93 −16	27
wisted (3) $\theta = 217°$ $\theta' = 217°$	3.71 −30	4.18 −28	3.79 −26	4.40 −21	4.43 +4	6.26 +41	3.65 −28	3.65 −23	3.71 −21	25
wisted (4) $\theta = 217°$ $\theta' = 37°$	3.71 −30	3.55 −39	3.76 −27	3.69 −24	3.81 −10	5.35 +20	3.65 −28	3.65 −23	3.71 −21	26

(continued on p. 272)

TABLE 4 (continued)

	II-1	*II-2*	*II-3*	*II-4*	*II-5*	*II-6*	*II-7*	*II-8*	*II-9*	*Av. ab diff. %*
R' =	*H*	*2'-F*	*2'-Me*	*2'-I*	*2',4'-Br_2*	*2',4'-$(NO_2)_2$*	*2',6'-Me_2*	*2',6'-$(iPr)_2$*	*2',4',6'-Br_3*	
Skew (2);	3.76	3.98	3.80	3.83	4.12	5.59	3.81	3.81	3.76	
$2\text{-}NO_2$ *proximal* $\theta = 180°$ $\theta' = 90°$	−29	−31	−26	−32	− 3	+26	−25	−19	−20	24
Skew (3);	3.86	4.16	3.86	4.13	3.57	4.97	3.72	3.72	3.87	
2'-R*distal* $\theta = 90°$ $\theta' = 0°$	−27	−28	−26	−26	−16	+12	−26	−21	−17	22
Skew (4);	3.86	4.60	3.73	4.51	4.09	5.59	3.72	3.72	3.87	
2'-R *proximal* $\theta = 90°$ $\theta' = 180°$	−27	−21	−27	−19	− 4	+26	−26	−21	−17	21
Butterfly,	3.86	5.29	3.47	4.99	5.01	6.89	3.66	3.66	3.81	
cis $\theta = 270°$ $\theta' = 90°$	−27	− 9	−32	−11	+18	+55	−28	−23	−19	25
Butterfly,	3.86	3.25	4.10	3.29	2.31	0.83	3.66	3.66	3.81	
trans $\theta = 90°$ $\theta' = 90°$	−27	−44	−20	−41	−46	−81	−28	−23	−19	37

* Difference from the measured dipole moment in %. The last column is the average of these differences di regarding sign.

In addition to those contained in Part I[38], the following assumptions were made:

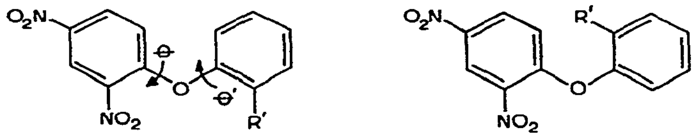
(1) The oxygen valency angle is 120° [27,34,43]. All other angles are also 120°.

(2) The group moments in benzene solution given by Smyth[44] are valid (C_{ar}–I = 1.30 D, C_{ar}–F = 1.46 D, C_{ar}–Br = 1.55 D, C_{ar}–Me = −0.4 D and C_{ar}–iPr = −0.4 D).

(3) A mesomeric moment of 1.31 D for the 2,4-dinitrophenoxy moiety acts at 20° from the O–C_1–C_4-axis toward C_3, as described in ref. 38. It is reduced by a factor of $\cos^2 \theta$ for an angle of rotation θ between the plane of the ring and the plane of the ether linkage. Even though the mesomeric moment for diphenyl ether (1.12–1.32 D[28,45]) is larger than for anisole (0.8–0.96 D[45]), the value of 1.31 D estimated from 2,4-dinitroaryl alkyl ethers is unlikely to be higher in these compounds. For the tetranitro ether (II-6) the mesomeric moment was assumed to act

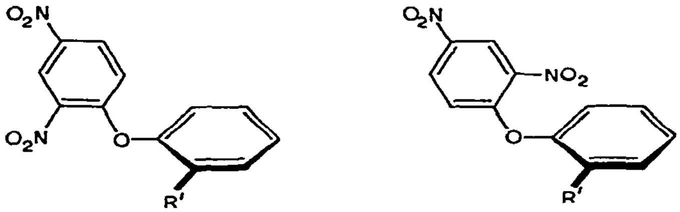
into both rings in accordance with the $\cos^2$ of the angle of rotation of either ring, such that the total mesomeric moment was never greater than 1.31 D.

Table 4 shows a comparison of the measured values and those calculated for the various conformations (Fig. 1) which have been proposed for diphenyl ethers. The conformations are defined by the twist angles θ and θ' shown in Fig. 1a. θ refers to the angle of rotation of the 2,4-dinitrophenyl ring about the C_1–O axis and θ' refers to the angle of rotation of the R′-phenyl ring about the $C_{1'}$-O axis. Both angles are zero when the molecule is in the Planar (1) conformation (Fig. 1a) and both angles are taken to rotate positively when the rings rotate clockwise, as viewed along the C_1–O or $C_{1'}$–O axes.



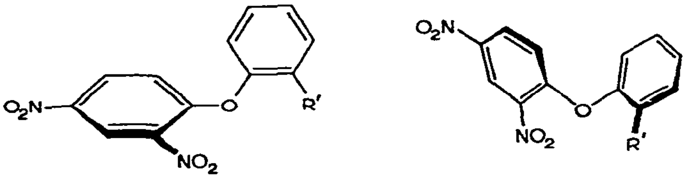
(a) Planar (1), *cis*
$\theta=0°$, $\theta'=0°$

(b) Planar (2), *trans*
$\theta=0°$, $\theta'=180°$



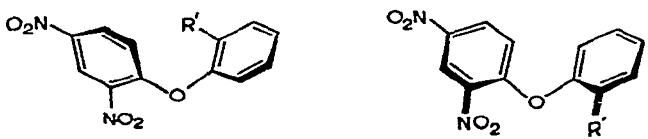
(c) Skew (1), 2-NO₂-*distal*
$\theta=0°$, $\theta'=90°$

(d) Skew (2), 2-NO₂-*proximal*
$\theta=180°$, $\theta'=90°$



(e) Skew (3), 2′-R-*distal*
$\theta=90°$, $\theta'=0°$

(f) Twisted (1)
$\theta=37°$, $\theta'=37°$



(g) Twisted (2)
$\theta=37°$, $\theta'=217°$

(h) "Butterfly", *cis*
$\theta=270°$, $\theta'=90°$

Fig. 1. Conformations of 2,4-dinitrophenyl R′-phenyl ethers.

Free rotations of one or both rings are not included in Table 4 because agreement with calculated values was pcor and because space-filling models* show them to be highly unlikely. The four *planar* conformations proposed in 1935[23], although impossible in space-filling models, are included because agreement was good in the case of two of them, Planar (1) and Planar (2). However, they are unlikely since steric hindrance presented by the 6-hydrogen to the 6′-substituent would make coplanarity very difficult[34,43]. Moreover, spectroscopic evidence has shown that diphenyl ether itself has only one plane of symmetry[7]. Planar conformations (3) and (4) in which the 2-nitro group overlaps the 2′-substituent or the 6′-hydrogen are even more unlikely and are in poor agreement with experiment.

Of the remaining possible conformations, the "*butterfly*", suggested by Smyth and Walls in 1932[22] in which both rings are perpendicular to the plane of the oxygen valency angle, is in poor agreement with the measured values. This is also true of two of the four *twisted* conformations and all but one of the *skew* conformations in Fig. 1.

Good agreement between measured and calculated dipole moments is obtained for the first four entries in Table 4. The structure in which there is *concerted rotation* ($\theta = \theta' + 90°$) has been proposed by Moir[14] and Fong[34]. The two twisted conformations, of the four possible, have been proposed by Le Fèvre and Saxby[36] on the basis of molar Kerr constants. In these conformations each ring is twisted from coplanarity in opposite directions by 37°. The four possible skew conformations first proposed by Morino in 1938[43] can be designated conveniently as *distal* and *proximal*[15] depending on the relation of the 2- or 2′-substituent to the other ring. Only the skew conformation with the 2-NO_2 *distal* shows good agreement.

Thus, the first four entries in Table 4 are all possible and a choice cannot be made between them on the basis of these measurements. The most logical conclusion is that the potential barrier is small and permits rotation of the dinitro ring about the C_1–O bond which, in turn, permits concerted rotation. Thus the doubly-bonded character of this link, which is responsible for the mesomeric moment, is not sufficient to constrain this motion at 25°. During concerted rotation all four skew conformations and close approximations to all four twisted conformations are generated. It is possible, due to the potential barrier plus Van der Waals forces, that greater populations of the Skew (1) and Twisted (1) and (2) forms are encountered within concerted rotation since their calculated dipole moment values are so similar that this would not affect the results. Including up to ±60° of oscillation in the non-conjugated (R′) ring in the skew conformations or up to 1.0 D of mesomeric moment along the $C_{1'}$–O bond into the R′ ring for all conformations in the calculations do not change these results significantly.

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* Corey–Pauling–Koltun space-filling models; cf. ref. 46.

ACKNOWLEDGMENTS

We wish to thank J. Guerrero and M. P. Gonzalez for their help in synthesizing the compounds used and M. Rioja for the determination of the dipole moments.

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