Dielectric Properties of Cyclic Nitramines and Related Compounds. Part I. Dipole Moments and Conformations of Nitramines, Nitrosamines, and 1,3,5-Trinitrocyclohexane

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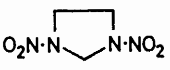
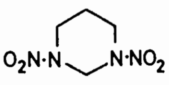
Dipole moments of 1,3,5-trinitrocyclohexane and various nitramines and nitrosamines have been determined in benzene and dioxan, and the resulting values are compared with values calculated from group moments and corresponding to possible conformations of the molecules. The experimental dipole moments (μ/D) are: 1,3-dinitroimidazolidine (I), 3·4 ± 0·2; 1,3-dinitroperhydropyrimidine (II), 5·6—5·75; 1,3-dinitroperhydro-1,3-diazepine (III), 5·15—5·25; 1,3,5,7-tetranitroperhydro-1,3,5,7-tetra-azocine (IV), 4·65 ± 0·05; bis-(3,5-dinitroperhydro-1,3,5-triazin-1-yl)methane (V), 7·15 ± 0·05; 1,3,5-trinitrosoperhydro-1,3,5-triazine (VI), *ca.* 3·8—4·5; 1,3-dinitro-5-nitrosoperhydro-1,3,5-triazine (VII), 5·5 ± 0·05; 3,7-dinitroso-1,3,5,7-tetra-azabicyclo[3.3.1]-nonane (VIII), 6·8 ± 0·4; 3,7-dinitro-1,3,5,7-tetra-azabicyclo[3.3.1]nonane (IX), 6·9 ± 0·3; 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane (X), 2·20—2·25; 1,3,5-trinitrocyclohexane (XI), 3·0 ± 0·2; and *N*-nitrosopiperidine (XII), 4·4 ± 0·05.

It has been shown[1] that compounds such as 1,3-dinitroperhydropyrimidine (II), 1,3-dinitroperhydro-1,3-diazepine (III), and 1,3,5-trinitrosoperhydro-1,3,5-triazine (VI) may be classified as 'globular' molecules and hence give rise to plastic crystal behaviour; the absence of this type of behaviour with the related compounds, 1,3-dinitroimidazolidine (I) and the well-known explosive 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) was discussed[1] in terms of factors affecting molecular rotation in the solid state. One such factor concerns the intermolecular forces in the crystal and how these may be influenced by the polar nature of the molecules. Consequently it was of interest to examine the dielectric properties of the compounds in question. We report here the results of dipole moment measurements, in solutions of non-polar solvents, of various nitramines and nitrosamines which are of interest in the explosives field. The compounds concerned are (I), (II), (III), 1,3,5,7-tetranitroperhydro-1,3,5,7-tetra-azocine (IV), bis-(3,5-dinitroperhydro-1,3,5-triazin-1-yl)methane (V), 1,3,5-trinitrosoperhydro-1,3,5-triazine (VI), 1,3-dinitro-5-nitrosoperhydro-1,3,5-triazine (VII), 3,7-dinitroso- (VIII) and 3,7-dinitro-1,3,5,7-tetra-azabicyclo[3.3.1]nonane (IX), 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane (X), 1,3,5-trinitrocyclohexane (XI), and *N*-nitrosopiperidine (XII).



(I)



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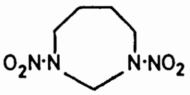

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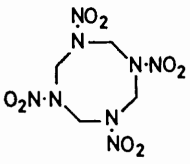

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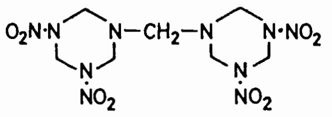

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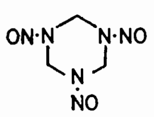
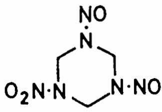
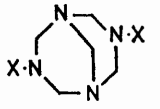


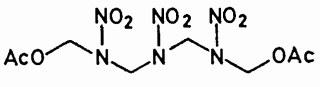
(VI)



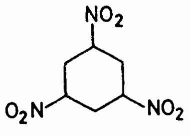
(VII)



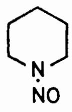
(VIII) X = NO
(IX) X = NO2



(X)



(XI)



(XII)

Wright[2] has reviewed the electrical polarisabilities of some nitramines, and dipole moment values for RDX in solution have been reported by George and Wright[3] and by Weisbecker and Rouquie.[4] Wright *et al.*[5] have investigated the dielectric properties of the polymorphs of compound (IV).

EXPERIMENTAL

Apparatus and Procedure.—Measurements of permittivity, refractive index, and density were carried out on at least five different concentrations of the solution under investigation. The relative permittivity was measured ($\pm 0{\cdot}001$) using either a 716 C General Radio bridge (1 kHz) in conjunction with a liquid dielectric cell DFL1, the latter supplied by Wissenschaftlich-Technische Werkstätten (WTW), or with a WTW dipolmeter, type DM01 (2 MHz) in conjunction with a WTW cell, also of type DFL1. Refractive index measurements at 298 ± 0·1 K were carried out using a high accuracy Abbé 60 refractometer, supplied by Bellingham and Stanley, using sodium D light; this gave an

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[1] P. G. Hall, *Trans. Faraday Soc.*, 1971, **67**, 556.

[2] G. F. Wright, 'Nitrocompounds,' Proceedings of the International Symposium, ed. T. Urbanski, Warsaw, 1963, p. 159; 'The Chemistry of the Nitro and Nitroso Groups,' ed. Feuer, Interscience, New York, 1969, ch. 9.

[3] M. V. George and G. F. Wright, *J. Amer. Chem. Soc.*, 1958, **80**, 1200.

[4] A. Weissbecker and A. Rouquie, *J. Chim. Phys.*, 1971, **68**, 910.

[5] M. Bedard, H. Huber, J. L. Myers, and G. F. Wright, *Canad. J. Chem.*, 1962, **40**, 2278.

error in n_D^2 of 0·0001. Density measurements ($\pm$0·0001 g cm^{-3}) were made at 298 ± 0·1 K with a Lipkin pyknometer.

The dipole moments were evaluated using the methods of Guggenheim and Smith,[6] Halverstadt and Kumler,[7] and Franchini.[8] (In some cases the distortion polarisation was estimated from relative permittivity measurements carried out directly on pressed discs of the solid, contained in a General Radio type 1690-A sample holder, and using the 716 C bridge; these results will be discussed in Part II.)

Materials.—Pure samples of compounds (I), m.p. 404 K, (II), m.p. 358·5 K, (III), m.p. 379 K, (X), m.p. 425—426 K, (IV), (IX), and RDX were supplied by E.R.D.E., Waltham Abbey.

The method of Bachman and Deno [9] was used to prepare compound (VI) with the quantities of the reactants scaled up. Compound (VI), m.p. 377·5 K, was recrystallised twice from distilled water to give yellow crystals. Compound (VIII) was prepared using the same method [9] except that the solution was buffered at pH 4 using potassium hydrogen phthalate; this nitroso-compound, m.p. 478—480 K, was recrystallised from methanol to give white crystals. Compound (V) was prepared [10] *via* 3,5-dinitroperhydro-1,3,5-triazine nitrate, the latter being prepared according to the method of Vroom and Winkler.[11] Compound (V) was recrystallised from acetone–light petroleum, m.p. 309 K (decomp.). Compound (VII) was prepared according to the method of Bell and Dunstan.[12] The pale yellow crystals were recrystallised from methanol, m.p. 441 K. Compound (XI) was prepared according to the method of Novikov *et al.*,[13] by reaction between 1,3,5-trinitrobenzene in tetrahydrofuran and sodium borohydride in 50% methanol at 271—275 K. The product was recrystallised several times from isopropanol to give white crystals, m.p. 391—392 K.

Dipole moments of some cyclic nitramines and nitrosamines

Solute	$\frac{T}{\text{K}}$	Solvent	$\frac{P_d}{\text{cm}^3\ \text{mol}^{-1}}$ (Discs)	$\frac{R_{2\infty}}{\text{cm}^3\ \text{mol}^{-1}}$ (Abbé)	$\frac{R_{2\infty}}{\text{cm}^3\ \text{mol}^{-1}}$ (Additive)	$\frac{P_{2\infty}}{\text{cm}^3\ \text{mol}^{-1}}$	$\frac{\mu_a}{\text{D}}$	$\frac{\mu_b}{\text{D}}$	$\frac{\mu_c}{\text{D}}$	$\frac{\mu_d}{\text{D}}$	$\frac{\mu_e}{\text{D}}$	$\frac{\mu_f}{\text{D}}$
(I)	298	Dioxan					3·4 ± 0·2	3·4 ± 0·2				3·36
(II)	298	Benzene					5·58	5·72				5·82
run 1	298	Dioxan					5·72	5·66				
	298	Dioxan	49·5	40·2	38·4	710·7	5·71	5·74	5·73	5·69	5·77	5·82
run 2	323	Dioxan				662·7			5·74	5·70		
(III)	298	Benzene					5·19	5·24				6·38
	298	Dioxan					5·24	5·15				
(IV)	298	Dioxan			58·3	503·9			4·67			
(V)	298	Dioxan [a]					7·13					7·15
(VI)	298	Benzene					4·48	4·47				5·57
	323	Benzene					4·51					
	298	Dioxan	52·4	39·6	38·0	364·7	3·97	3·98	3·99	3·91		
	323	Dioxan				325·7			3·90	3·81		
(VII)	298	Benzene			41·8	667·3			5·53			6·14
(VIII)	298	Dioxan	61·6		44·9	983·1			6·8 ± 0·4			7
(IX)	298	Dioxan [a]					6·9 ± 0·3					8
(X)	298	Dioxan [a]					2·20	2·25				2·30
(XI)	298	Benzene					3·0 ± 0·2					2·97
(XII)	298	Benzene			31·2	424·5			4·39			

μ_a, Dipole moment determined using Guggenheim–Smith [6] equation, linear plots and measured values of ε_{r1} and n_1^2. μ_b, Dipole moments determined using Guggenheim–Smith [6] equation, the extrapolation ($w_2 \longrightarrow 0$) of $(\varepsilon_{r12} - \varepsilon_{r1}/w_2)$, and $(n_{12}^2 - n_1^2)/w_2$ and using measured values of ε_{r1} and n_1^2; where ε_r is the relative permittivity, n^2 is the square of the refractive index and the subscripts, 1, 2, and 12 refer to solvent, solute, and solution respectively. w_2 is the weight fraction or mole fraction of the solute. μ_c, Dipole moment determined using Halverstadt and Kumler [7] method and either $R_{2\infty}$ (additive) or $R_{2\infty}$ (Abbé) as the molar refraction. μ_d, Dipole moment determined using Halverstadt and Kumler [7] method and using P_d (discs) as the distortion polarisation. μ_e, Dipole moment determined by Franchini [8] method. μ_f Calculated dipole moment.

[a] AnalaR dioxan.

Purification of Solvents.—AnalaR benzene was refluxed with P_2O_5 for 8 h using a circulatory drying apparatus; on each cycle the benzene was passed through a drying tube containing Linde molecular sieves, type 4A. The fraction boiling at 353·1 K was stored over freshly prepared sodium wire, n_D 1·42350 ± 0·00004. AnalaR dioxan was refluxed with sodium for 50 h. Fresh sodium metal was added periodically until the floating globules remained untarnished. The fraction boiling at 374 ± 1 K gave n_D 1·42019 ± 0·00004 and was always used immediately following purification.

RESULTS AND DISCUSSION

The experimental values of the dipole moments obtained using the methods of Guggenheim and Smith [6] (μ_a, μ_b), Halverstadt and Kumler [7] (μ_c, μ_d), and Franchini [8] (μ_e) are compared in the Table with the calculated values (μ_f), and the various possible conformations of the molecules are shown in Figures 1—4.

Values of μ_f were calculated by vector addition of the individual group moments. Ring geometries were generally calculated using the following bond angles [14] and lengths [14]: $\widehat{CNC}$, 120°; $\widehat{CCC}$, 109° 28′; C–N, 0·145 nm; C–C, 0·154 nm. However for (I) it was assumed that $\widehat{CNC} = \widehat{CCC} = 108°$.

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[6] J. W. Smith, 'Electric Dipole Moments,' Butterworths, London, 1955, p. 60.

[7] I. F. Halverstadt and W. D. Kumler, *J. Amer. Chem. Soc.*, 1942, **61**, 2988.

[8] P. F. Franchini, *Trans. Faraday Soc.*, 1967, **63**, 2610.

[9] W. E. Bachman and N. C. Deno, *J. Amer. Chem. Soc.*, 1951, **73**, 2777.

[10] E. M. Smolin and L. Rapoport, '*s*-Triazines and Derivatives,' Interscience, New York, 1959, p. 515.

[11] A. Vroom and C. Winkler, *Canad. J. Res.*, 1950, **28***B*, 701.

[12] J. A. Bell and I. Dunstan, *J. Chem. Soc.* (*C*), 1966, 862.

[13] S. S. Novikov and L. J. Nitsku Schmel, *Izvest Akad. Nauk. S.S.S.R. Ser. khim., U.S.S.R.*, 1970, **11**, 2639.

[14] A. Filhol, C. Clement, M. Forel, J. Paviot, M. Rey-Lafon, G. Richoux, C. Trinquecoste, and J. Cherville, *J. Phys. Chem.*, 1971, **75**, 2056.

The group moments of N–NO_2 and N–NO were taken as being equal to the dipole moments[3] of dimethylnitramine (4·61 D) and dimethylnitrosamine (4·01 D) respectively; dimethylnitramine[15] and dimethylnitrosamine[16] have been shown to have planar structures. For compound (XI) the C–NO_2 group moment was assumed to be the same as the dipole moment (3·2 D) of nitromethane, and the $\widehat{NCH}$ angle was taken as 108°. The group moment[17] of the lone pair electrons on the nitrogen atoms in compound (V) was taken as 0·8 D.

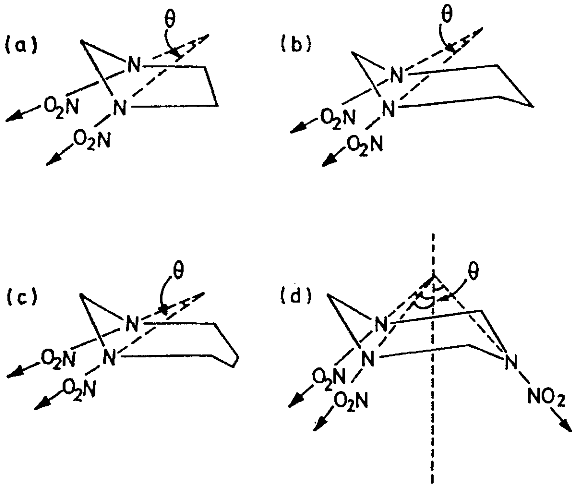

FIGURE 1 Conformations of compounds (I)—(III) and RDX: (a) (I), θ = 135° 14′, μ_{calc} = 3·36 D; (b) (II), θ = 101° 30′, μ_{calc} = 5·82 D; (c) (III), θ = 92° 28′, μ_{calc} = 6·38 D; (d) RDX, θ = 62° 20′, μ_{calc} = 6·42 D

In the Table, unless otherwise is stated, the error limits for the experimental values of μ are ± *ca.* 0·05 D.

Compounds (I)—(III) *and RDX*.—For compound (I), the calculated dipole moment shows good agreement with the experimental value; thus the conformation shown in Figure 1 seems the most probable. This type of envelope conformation has been proposed for *cis*-1,3-dimethylcyclopentane.[18] The calculated dipole moment for a planar conformation of compound (I) is *ca.* 2·9 D.

Compound (II) was assumed, like RDX (see below), to exist in a chair conformation, and the resulting calculated dipole moment (5·8 D) shows reasonably good agreement with the experimental values (5·58—5·77 D). The latter may be compared with the experimental dipole moments[3] of RDX (5·78 D) and 3,5-dinitroperhydro-2*H*-1,3,5-oxadiazine (5·64 D). It is interesting that compound (II) and RDX have dipole moments of about the same magnitude.

The calculated dipole moment for compound (III) is significantly higher than the experimental values, which may be explained by the molecule existing in a skew chair or twist chair form as in cycloheptane.

The experimental dipole moments of compounds (II)

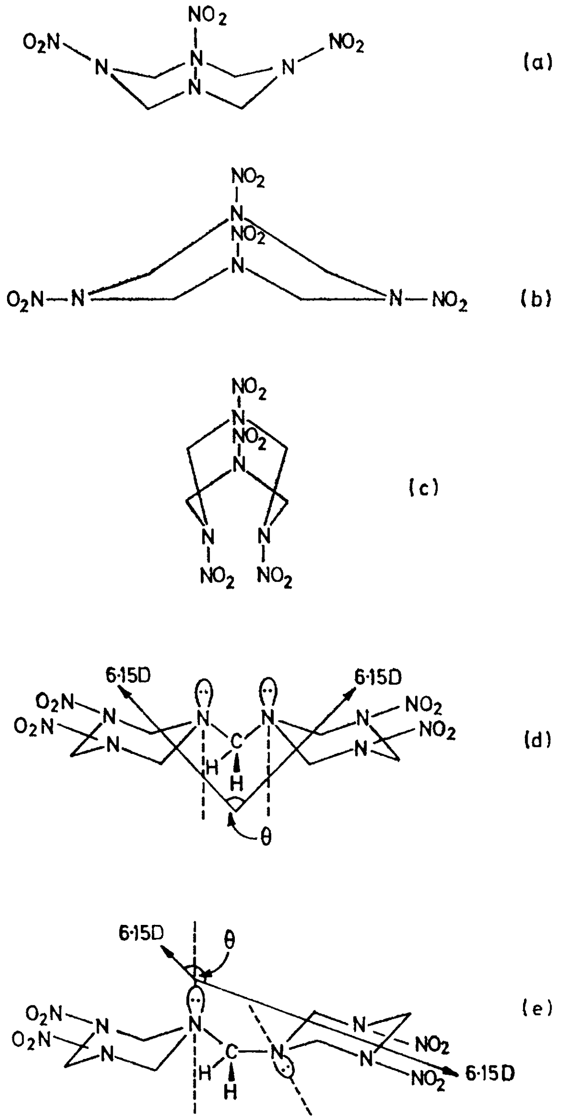

FIGURE 2 Conformations of compounds (IV) and (V): (a) (IV) (α), μ_{calc} = 15·04 D; (b) (IV) (γ), μ_{calc} = 9·22 D; (c) (IV) (β), μ_{calc} = 0 D; (d) (V), θ = 72° 14′, μ_{calc} = 10·1 D; (e) (V), θ = 109° 28′, μ_{calc} = 7·15 D

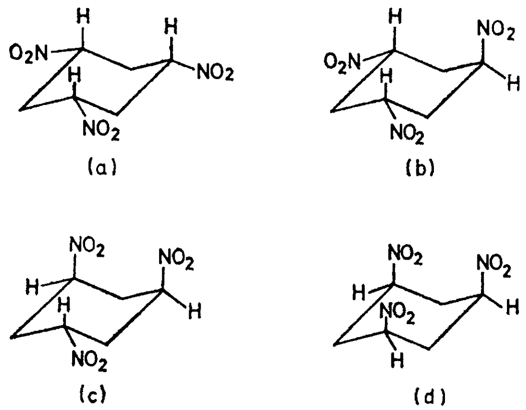

FIGURE 3 Conformations of compound (XI): μ_{calc} = (a), (b) 2·97 D; (c) 6·21 D; (d) 9·6 D

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[15] W. Costain and E. G. Cox, *Nature*, 1947, **160**, 826.

[16] P. Rademacher and R. Stoelevik, *Acta Chem. Scand.*, 1969, **23**, 660.

[17] R. J. Bishop, L. E. Sutton, D. Dineen, R. A. Y. Jones, A. R. Katritzky, and R. J. Wyatt, *J. Chem. Soc.* (*B*), 1967, 493.

[18] J. N. Haresnape, *Chem. and Ind.*, 1953, 1091.

and (III) do not change significantly when measured in the different solvents, benzene and dioxan; also, for compound (II), the experimental dipole moment shows good agreement among the various different methods [6-8] of evaluation.

Filhol *et al.*[14] have studied the molecular structure of RDX suggesting that it exists in solution as a chair conformation having C_{3v} symmetry; they calculated (by INDO) a value of μ of 5·48 D which may be compared with our calculated value of 6·4 D and with the experimental values of 5·78 D in dioxan [3] and *ca.* 7 D in polar solvents.[4]

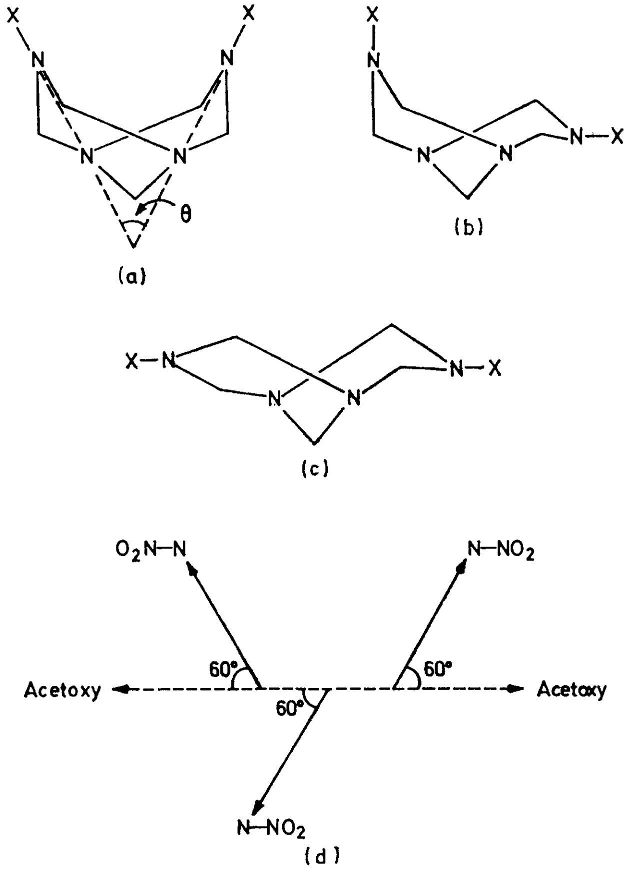

FIGURE 4 Conformations of compounds (VIII); X = NO) and (IX; $X = NO_2$) (a)—(c) and (X) (d)

Compounds (IV) *and* (V).—The measured value (4·67 D) of the dipole moment of compound (IV) in dioxan agrees closely with the value of 4·68 D reported by Wright *et al.*,[5] who suggested structures of the type Figure 2(a)—(c) for three of the polymorphs of compound (IV). However, none of the calculated dipole moments (Figure 2), *i.e.* 0, 9·22, 15·04 D is in agreement with the experimental value. Wright *et al.*[5] detected conformational motion in the α and γ polymorphs of compound (IV), so that in the absence of lattice forces it is feasible that compound (IV) will undergo rapid conformational changes in solution; the observed dipole moment would then be the statistical average of the moments of the conformers present.

For compound (V), two possible conformations [Figure 2(d) and (e)] which had the least steric hindrance were considered, and moments were calculated on the assumption that each half of the molecule existed in a chair conformation, as in compound (II). Of the resulting values, 7·15 and 10·1 D, the former agrees closely with the experimental value of 7·1 D; consequently this particular structure is the preferred one.

Compound (XI).—Four chair conformations (Figure 3) are possible in this case, but the calculated moments for only two of these [(a) and (b)] correspond to the experimental value (3·0 ± 0·20 D). Thus, compound (XI) probably exists in solution as either one of the conformers (a) and (b), or a mixture of the two. 1,3,5-Trimethylcyclohexane [19] has been considered to exist as an equilibrium mixture of two conformers, one with three equatorial methyl groups, and the other with two equatorial and an axial methyl group.

Compounds (VIII) *and* (IX).—The measured dipole moments of (VIII) and (IX) were 6·8 and 6·9 D respectively. If these molecules had flexible structures, the dipole moments would be expected to be similar in magnitude to the values [3] for *NN'*-dinitrosopiperazine (2·08 D) and *NN'*-dinitropiperazine (2·21 D). However, the comparatively high values suggest fixed structures such as that shown in Figure 4(a) which corresponds to calculated values of *ca.* 7 for compound (VIII) and *ca* 8 D for compound (IX). Two other possible conformations for compounds (IX) and (VIII) are shown in Figure 4 (b) and (c). However, the calculated values for conformation (c) are *ca.* 0 D and for (b) they are *ca.* 4 for compound (VIII) and *ca.* 4·6 D for compound (IX). Thus, structure (a) is the only one of these which is compatible with the experimental dipole moments; such a structure is not one of the preferred conformations of the cyclo-octane ring, but the bridging methylene group in compounds (VIII) and (IX) should add rigidity to the molecules.

Compounds (VI) *and* (VII).—The calculated dipole moments for compounds (VI) and (VII) in chair conformations as in RDX are 5·57 and 6·14 D respectively, *i.e.* both significantly higher than the experimental values. The difference is greater for compound (VI) [for compound (VII) the difference between the calculated and experimental values is about the same as that for RDX] but some difficulty was experienced in obtaining clear solutions of this compound, and corrections for up to *ca.* 1% undissolved solid had to be applied to the weight fractions; thus, the experimental value for compound (VI) must be treated with less confidence than the other experimental values and no great significance can be attached to the difference in results between benzene and dioxan.

Compound (X).—Examination of a molecular model of compound (X) shows that there would be appreciable steric hindrance with a ring type of structure, a linear chain structure being more feasible. The experimental dipole moment is 2·20—2·25 D and the simplest structure

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[19] C. J. Egan and W. C. Buss, *J. Phys. Chem.*, 1959, **63**, 1887.

[Figure 4(d)] corresponding to this, with a calculated value of 2·3 D, involves the nitramine groups inclined at 60° to a central axis and inclined at 120° to each other; the acetoxy-group moments are assumed to cancel each other.

In conclusion, the calculation of dipole moments for the proposed conformations by relatively simple vector addition gives reasonable agreement with experimental values in many cases. No account has been taken of the possible effects of one-sided conformational equilibria and of changes in the calculated moment with changes in dimensions.

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