Molecular Polarisability. The Conformation of *NN'*-Dinitropiperazine and Other Cyclic Nitroamines in Dioxan Solution

By **Kingsley E. Calderbank*** and **Raymond K. Pierens**, School of Chemistry, University of Sydney, N.S.W., 2006, Australia

Dipole moments and molar Kerr constants are reported for dimethylnitroamine, *N*-nitropiperidine, *N*-nitromorpholine, *NN'*-dinitropiperazine, 3,7-dinitro-1,3,5,7-tetra-azabicyclo[3.3.1]nonane, 1,3,5-trinitro-1,3,5-triazacyclohexane, and 1,3,5,7-tetranitro-1,3,5,7-tetra-azacyclo-octane at 25 °C. The effective molecular polarisability anisotropies are derived for dimethylnitroamine and the values obtained used to investigate the possible solution conformations of the monocyclic secondary nitroamines.

THIS paper is concerned with the application of polarity and polarisability considerations to the examination of solution-state conformations of cyclic nitroamines. Parameters derived from the measured dipole moments and molar Kerr constants of dimethylnitroamine (DMN) and 3,7-dinitro-1,3,5,7-tetra-azabicyclo[3.3.1]-nonane (DPT) are used to deduce the conformations in solution of *N*-nitropiperidine, *N*-nitromorpholine, and *NN'*-dinitropiperazine, and are then applied to the more complex situations of 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetra-azacyclo-octane (HMX).

EXPERIMENTAL

Materials, Apparatus, etc.—The nitroamines DMN,[1] *N*-nitropiperidine,[1] *N*-nitromorpholine,[2] *NN'*-dinitropiperazine,[3] and DPT [4] were prepared according to the literature methods cited. RDX and HMX were purified from samples obtained from the Munitions Factory, Australian Department of Supply. Dioxan solvent was purified by partial freezing and storage over sodium. The apparatus, techniques, symbols used, and calculation procedures have been described before.[5] For $w_2 = 0$ the following solvent constants apply: $\varepsilon_1 = 2.209\,0$; $d_1 = 1.028\,0$; $n_1 = 1.420\,2$; and $10^7 B_1 = 0.068$. The experimental results are summarised in Table 1. The molar refraction for HMX was not determined in this work because of a severe solubility limitation and the estimate given in the Table has been obtained from the relation $R_D(\text{HMX}) = \frac{4}{3}R_D(\text{RDX})$. The dipole moments ($\mu$) and molar Kerr constants (${}_mK$) are given in S.I. units. The conversion factors from the electrostatic system are respectively: 1 C m = $0.299\,8 \times 10^{30}$D, and 1 m^5 V^{-2} mol^{-1} = $0.898\,8 \times 10^{15}$ e.s.u. mol^{-1}.

Previous Measurements.—The molar Kerr constants for all the solutes of Table 1 together with the dipole moments for *N*-nitropiperidine and DPT have not been reported previously. Apart from HMX the previous dipole moment determinations listed in ref. 6 for the remaining solutes are in reasonable agreement with those of the present work.

TABLE 1

Refractions, polarisations, dipole moments, and molar Kerr constants (from observations on dioxan solutions at 25°C)

Solute	$10^5 w_2$ (no. of solns. measured)	$\alpha\varepsilon_1$	β	γ	δ	R_D/ cm^3	P_2/ cm^3	10^{30}* μ/ C m	$10^{27}{}_\infty(\text{m}K_2)$/ m^{5}V^{-2} mol^{-1}
DMN	635—2 697 (5)	28.2	0.107	0.029	534	23	442	15.08 ± 0.05	607 ± 5
N-Nitropiperidine	984—2 592 (5)	20.4	0.106	0.039	415	34	471	15.39 ± 0.10	683 ± 10
N-Nitromorpholine	408—1 237 (3)	9.56	0.173	0.063	185	34	240	10.54 ± 0.07	307 ± 10
NN'-Dinitropiperazine	410—639 (8)	4.30	0.307	0.082	−74.9	42	161	7.95 ± 0.10	−173 ± 3
DPT	130—247 (6)	29.0	0.374	0.12	387	54	1 083	23.6 ± 0.3	1 052 ± 18
RDX	256—727 (8)	18.6	0.374	0.070	−282	47	720	19.1 ± 0.15	−831 ± 15
HMX	61—133 (6)	12.0	0.409	*ca.* 0	−25.6	(63) †	637	17.7 ± 1.0	−117 ± 46

* Calculated on the basis that ${}_DP = 1.05\,R_D$. † See text.

DISCUSSION

N-*Nitropiperidine*, N-*Nitromorpholine, and* NN'-*Dinitropiperazine*.—In order to deduce the solution conformations of *N*-nitropiperidine, *N*-nitromorpholine, and *NN'*-dinitropiperazine we first derived the molecular polarisability anisotropy for dimethylnitroamine. This can be obtained from a consideration of the molar refractions, polarities, and molar Kerr constants of DMN and DPT. Structural evidence [7] for DMN indicates that the C_2NNO_2 grouping is planar. Hence the moment of DPT can be considered to be the resultant of the vector product of two coplanar trimethylamine moments,[8] each acting at 70.5° to the principal major axis, and the vector product of two dimethylnitroamine moments each acting at (180 — θ)° to the same molecular axis. Use of the measured moment of DPT in Table 1 gives a value for θ of 33° ± 1°.

We assume that an ellipsoid of polarisability (defined by the polarisability semi-axes b_1, b_2, and b_3) is associated with each of the molecules studied. For dimethylnitroamine orthogonal principal axes (1, 2, and 3) exist, such that axes 1 and 2 lie in the C_2NNO_2 plane with 1 parallel to the molecular dipole moment direction. Using the polarisability parameters for trimethylamine [8] and assuming the CH bond to be isotropically polarisable ($b_i = 0.72$ †),[9] expressions can now be written [10] for the ${}_mK$ of DPT, and for ${}_EP$ (= $0.95R_D$) and ${}_mK$ of DMN involving the unknown molecular polaris-

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† The polarisability semi-axes are expressed throughout as 10^{-40} C m^2 V^{-1}.

ability semi-axes for dimethylnitroamine. Solution of the equations gives $b_1 = 11.3$, $b_2 = 10.0$, and $b_3 = 7.2$.

Conformational investigations of *N*-nitropiperidine, *N*-nitromorpholine, and *NN'*-dinitropiperazine involve consideration of chair and flexible ring arrangements. For these molecules we have taken the CNC angle and the N–C bond length to be 114° and 1.41 Å respectively, these values being taken from the listings for DMN and 1,2-bis-(*N*-nitroamino)ethane in Sutton's compilation.[7] For these and subsequent $_{\mathrm{m}}K$ calculations the following bond parameters are needed: $b_{\mathrm{L}}(\mathrm{C{-}H}) = b_{\mathrm{T}}(\mathrm{C{-}H}) = b_{\mathrm{V}}(\mathrm{C{-}H}) = 0.72$,[9] $b_{\mathrm{L}}(\mathrm{C{-}C}) = 1.08$, $b_{\mathrm{T}}(\mathrm{C{-}C}) = b_{\mathrm{V}}(\mathrm{C{-}C}) = 0.29$,[9] $b_{\mathrm{L}}(\mathrm{C{-}O}) = 0.73$, and $b_{\mathrm{T}}(\mathrm{C{-}O}) = b_{\mathrm{V}}(\mathrm{C{-}O}) = 0.51$.[11]

The calculated dipole moments for the chair and flexible (twist boat) forms for *N*-nitropiperidine do not vary significantly with conformation. Using the observed dipole moment, $_{\mathrm{m}}K$(calc.) values for the chair and the 1,4-twist boat conformers are +683 and +879 respectively, the former being in excellent agreement with $_{\mathrm{m}}K$(obs.) (+683; see Table 1). The expected molar Kerr constants for the 2,5-twist species, although this could not be calculated here owing to insufficient structural parameters, would be much lower than that observed.

In the case of *N*-nitromorpholine additional structural parameters[11] are required. These are the COC angle (= 110°) and the COC moment (= 4.40). Dipole moment calculations do not distinguish between the chair form and that flexible conformation which retains bond angle and bond length requirements and is produced by twisting the chair about the 1,4-axis. The calculated molar Kerr constants for the chair and this twist-boat are +415 and +315 respectively. The experimental value (307 ± 10, Table 1) therefore indicates the twist boat conformation for *N*-nitromorpholine in dioxan solution.

An extension of these computational procedures to *NN'*-dinitropiperazine produces the interesting situation that μ(calc.) for the chair conformer (earlier shown to be applicable to *N*-nitropiperidine) and for the flexible form produced by twisting a model of the chair form about the 1,4-axis (the conformer applicable to *N*-nitromorpholine) are both zero, and consequently both have small positive Kerr constants. These results are to be compared with the μ(obs.) and $_{\mathrm{m}}K$(obs.) of 7.95 and −173 respectively. Polar flexible forms, however, are obtained by twisting the chair structure about the 2,5-axis. The calculated molar Kerr constant for that particular twist structure which yields the observed dipole moment is −192. In view of the conclusions of Wright[3,12] that *NN*-dinitropiperazine (a) is not centrosymmetric in the crystal lattice and (b) is not to be described adequately by static structures we must conclude that if the solution state of *NN'*-dinitropiperazine is not adequately described by the single static structure indicated above, then that structure (within the inherent limitations of time scale of our experimental techniques) must be the predominant contributor to a dynamic equilibrium.

The Nitro-aza-heterocycles RDX and HMX.—The molecule RDX is a six-membered ring species composed of three C_2NNO_2 units. In this case molecular models indicate that chair, twist-boat, and boat forms must be considered. Assuming tetrahedral angles about each carbon, and using structural parameters given earlier, dipole moments and molar Kerr constants are calculable for these forms. The results are summarised in Table 2.

TABLE 2

Calculated dipole moments and molar Kerr constants for RDX

	μ(calc.)	$_{\mathrm{m}}K$(calc.)
Chair	22.27	−2 868
	(19.1)	(−2 102)
Boat	5.81	+172
Twist-boat	7.04	+164

In the calculation of the dipole moment for the chair conformer we have used the observed moment of DMN to represent the polarity of the C_2NNO_2 group and therefore it is probable that the value obtained (22.27) is an overestimate. For this reason Table 2 contains a $_{\mathrm{m}}K$(calc.) for the chair structure obtained using the observed dipole moment (19.1). Clearly no single static structure gives agreement between observed and calculated values and any mixture of these forms (from dipole moment considerations) must have a minimum of 70% of the chair form. However, such a mixture gives a resultant molar Kerr constant far more negative (*ca.* −2 000) than that observed (−831). Although our results are inconclusive it would appear that in any mixture of conformers the chair form will predominate.

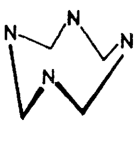
The eight-membered ring-system of HMX considerably increases the number of possible conformers to be examined and also increases the complexity of the calculations.[13] From a consideration of the models of HMX corresponding to Hendrickson's nine forms of cyclo-octane with definable symmetry, some of these can be eliminated by steric arguments. We have retained the identification numbering system of Hendrickson, but it should be noted that for each of (II), (IV), (V), and (VII) there are two isomers owing to the presence of the alternate carbon and nitrogen atoms in the rings. The ' A ' form has been designated arbitrarily to be that isomer with a nitrogen at ring position 1 [see (IIA) and (IVA)]. For the forms not eliminated by steric arguments we have calculated the dipole moments and molar Kerr constants and the results are summarised in Table

TABLE 3

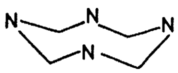
Calculated dipole moments and molar Kerr constants for HMX

	μ(calc.)	$_{\mathrm{m}}K$ (calc.)
(I)	49.2	+6 430
(IIA)	30.2	−1 282
(III)	See text	See text
(IVA)	21.3	+1 247
(VA)	0	Small +ve
(VI)	0	Small +ve
(VIIA)	0	+ 53.4
(VIII)	0	Small +ve
(IX)	See text	See text

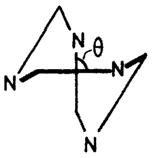
3. Kerr constants for some of the forms were not calculable because of insufficient parameters for the ring; however, those forms which from symmetry are non-polar [(VA), (VI), and (VIII)] must have a ${}_{\mathrm{m}}K$(calc.) which is small and positive (estimated to be 55 ± 15). Form (III) can be considered as two four-atom planar segments with a dihedral angle θ; where $\theta = 90°$ the structure will have zero dipole moment and consequent small positive ${}_{\mathrm{m}}K$. However, this particular form cannot have standard sp^2(N) and sp^3(C) bond angles around nitrogen and carbon. If θ is varied to allow these angles to have their standard values then the conformer becomes increasingly polar and its Kerr constant more negative. It seems apparent that there would exist a value of θ that yields a μ(calc.) and ${}_{\mathrm{m}}K$(calc.) close to that observed. A similar situation exists for (IX). If $\phi = 0°$ then the non-polar form (VI) results. An examination of the model suggests that there exists a value of ϕ to give calculated and observed quantities in reasonable agreement. Table 3 indicates that none of the individual remaining forms can represent HMX in solution. It should be noted that (IVA) (μ 21.3) has a moment closest to that measured (17.7). A small distortion could slightly lower the moment and produce a negative Kerr constant.



(I)



(IIA)



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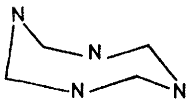
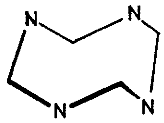
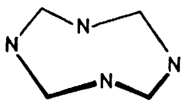


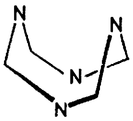
(IVA)



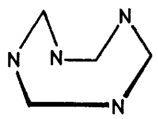
(VA)



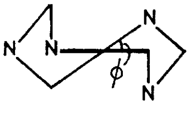
(VI)



(VIIA)



(VIII)



(IX)

If HMX exists in solution as a mixture of rigid forms, some generalisations can be made. First it is clear that the 'crown' (I) will not be a significant contributor. Secondly, the non-polar forms and those with large negative Kerr constants at best will be minor contributors to any conformational mixture. In summary, our observations are consistent with a single structure, or a group of structures with conformations of the 'boat–chair' [(IVA) and (IX)] and the 'chair–chair' [(IIA) and (III)] types. N.m.r. studies indicate that a dynamic equilibrium must exist. From ^{1}H-n.m.r. spectra we calculate, using the coalescence temperature method, the energy of activation for this inversion, $\Delta G^\ddagger$ (−98 °C), to be 34.5 kJ mol^{-1} in [$^2H_6$]acetone. Because of this low energy barrier to inversion and the inherent long time-constant of our experimental techniques it is probable that a dynamic equilibrium would appear as a single structure or as groups of structures intermediate between the extremes, and so the generalisations in the foregoing summary can be applied also to the dynamic picture.

Because of solubility limitations, we have been restricted to the use of dioxan as solvent. It is known [14] that significant differences often exist between the dipole moments of nitrogen-containing solutes measured in dioxan and those in other non-polar solvents. However, these solutes usually have a hydrogen atom attached to the nitrogen and, hence, are able to form complexes containing a weak hydrogen bond of the type N–HO-(dioxan). With the solutes of the present study no such H-bonding is possible. Further, the dioxan molecule is almost isotropically polarisable and, therefore, in the preceding discussions we have assumed that solute–solvent interactions are unimportant.

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