Rotational Barriers in 2-Dimethylamino-1,3,4-oxadiazoles and -thiadiazoles. A CNDO/2 Study

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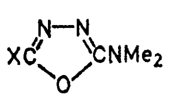
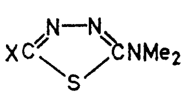
The barriers to rotation of the dimethylamino-group in a series of 5-substituted 2-dimethylamino-1.3.4-oxadiazoles and -thiadiazoles have been calculated by the CNDO/2 method with and without *d*-orbitals in the basis set for sulphur. When a planar dimethylamino-nitrogen atom is employed, the experimental barriers are very satisfactorily reproduced, but when allowance is made for a pyramidal nitrogen atom, quite unrealistic results are obtained. The effects of *d*-orbitals and of pyramidalisation are analysed and discussed.

THE existence of a barrier to internal rotation of an amino- or substituted amino-group attached to a conjugated or aromatic system is classically attributed to resonance interaction between the lone pair of the amino-nitrogen atom and the remaining π-electron system. Experimentally such barriers have been found in amides, thioamides, amidines, and similar classes of compounds.[1,2] Barriers to internal rotation have also been observed in aromatic compounds such as anilines,[3] amino-pyridines,[4] and -pyrimidines.[5] In a few cases this type of rotational barrier has been studied theoretically by semiempirical all-valence-electron methods. Shaw and Reeves [6] have carried out CNDO/2 calculations on formamide and Almog and Meyer [5] have performed analogous calculations on 4-dimethylamino-pyrimidine, -quinazoline, and -pyrido[3,2-*d*]pyrimidine. Some of these calculations were, however, complicated by steric phenomena.

We have recently observed and measured barriers to internal rotation around the exocyclic carbon–nitrogen bond in various 2-dimethylamino-1,3,4-oxa- and -thiadiazoles.[7]

In these compounds the rotational barriers are not complicated by steric factors and should therefore reflect the electronic interaction between the dimethylamino-group and the heterocyclic ring. For this reason we found it interesting to investigate the ability of the CNDO/2 method to treat this interaction as it shows up in the rotational barriers of compounds (I) and (II). The investigation also includes the effect of sulphur 3*d*-orbitals on the calculated barriers of compounds (IIa—f), and a study of the influence of different geometries around the exocyclic nitrogen atom.


(I)


(II)

a; $X = NO_2$
b; $X = CN$
c; $X = CO_2Et$

d; $X = CF_3$
e; $X = H$
f; $X = Ph$

A standard CNDO/2 program [8] was used for all calculations, except for those performed with the *sp*

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[1] G. Binsch, *Topics Stereochem.*, 1968, **3**, 132.

[2] H. Kessler, *Angew. Chem.*, 1970, **82**, 237.

[3] R. K. MacKenzie and D. D. MacNicol, *Chem. Comm.*, 1970, 1299.

[4] A. R. Katritzky and G. J. T. Tiddy, *Org. Magnetic Resonance*, 1969, **1**, 57.

[5] J. Almog, A. Y. Meyer, and H. Shanan-Atidi, *J.C.S. Perkin II*, 1972, 451.

[6] K. N. Shaw and L. W. Reeves, *Chem. Phys. Letters*, 1971, **10**, 89.

[7] T. Liljefors, to be published.

[8] J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970, appendix A.

approximation for sulphur. In this latter case a revised CNDO/2 program was employed.[9,10]

Geometry of the Molecules.—Bond angles and bond distances for the ring structures have been taken from microwave determinations.[11,12] These values were assumed to be unchanged by substitution. The geometries of the substituents X have been constructed from values in ref. 13 and are summarised in Table 1.

TABLE 1

Geometries of the substituents X

X	Bond distances (Å)		Bond angles (°)	
NO_2	C(ring)–N	1·49	C–N–O	118
	N–O	1·21	O–N–O	124
CN	C(ring)–C	1·42		
	C–N	1·16	C–C–N	180
CO_2Et	C(ring)–C	1·48	O–C–O	122
	C=O	1·23	C–C=O	121
	C–O	1·31	C–C–O	117
	CH_2–O	1·51	C–O–CH_2	117
	CH_2–CH_3	1·55	All other angles	109·47
	C–H	1·08		
CF_3	C(ring)–C	1·52	All angles	109·47
	C–F	1·33		
H	C(ring)–H	1·08		
Ph	C(ring)–C	1·45		
	C–C	1·397	All angles	120
	C–H	1·08		

Since different bond angles around the amino-nitrogen atom have been used in the calculations, these are given as parameters shown in Figure 1.

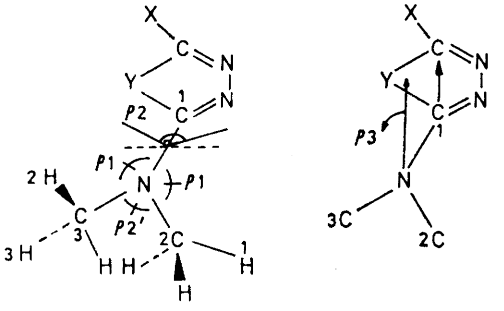

FIGURE 1 Definition of the parameters used in the description of the geometry and rotation of the dimethylamino-group (Y = O or S)

*P*1 and *P*2′ are bond angles in the dimethylamino-group, and *P*2 is the angle between the planes through C(1)NC(2) and C(1)NC(3). *P*3 is the angle between a plane perpendicular to the ring and a plane through C(1)N and bisecting the C(2)NC(3) angle. *P*3 describes the rotation of the dimethylamino-group. In all calculations the N–Me bond length is 1·46 and the C–H bond length 1·08 Å.

The two methyl groups have been kept in the staggered conformation shown in Figure 2(a), with bond angles of 109·47°. This is the simplest conformation to handle when *P*2 is given different values, since the ' cog-wheel ' situation is then preserved. However, this conformation may not correspond to the state with lowest energy.[5,14] To obtain an estimate of the error introduced by adopting the ' cog-wheel ' conformation,

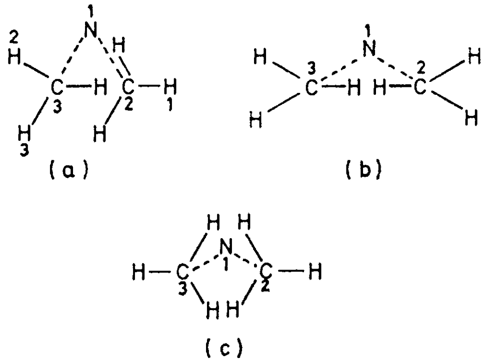

FIGURE 2 The methyl group conformations of the dimethylamino-group used in the energy calculations

calculations were made with *P*1 = 120, *P*2 = 180, and *P*3 = 0° and with the methyl groups in two other reasonable conformations, shown in Figures 2(b) and (c). Compared to the ' cog-wheel ' conformation, that shown in Figure 2(b) destabilises the molecule by 3·3 kJ mol^{-1}, while that in Figure 2(c) leads to a stabilisation by 2·1 kJ mol^{-1}. The latter conformation, however, introduces problems with H–H interactions when *P*2 is varied, and to avoid an excess of computational work with different methyl rotamers, the small energy difference was neglected and the staggered conformation [Figure 2(a)] was used throughout the calculations.

Since the calculated barriers are expected to be significantly sensitive to the exocyclic carbon–nitrogen bond length, and since this bond length is also expected to be different for *P*3 = 0 and 90°,[15] we found it necessary to use a geometrical optimisation procedure in this case, which was performed in the following way. Two compounds in each series (Ia), (Ie), (IIa), and (IIe) were chosen, representing the extremes of electron-withdrawing capacity among the substituents under consideration. For *P*1 = 120, *P*2 = 180, and *P*3 = 0°, energy values for at least five different C–N bond lengths were calculated. Parabolas were least-squares fitted to the energy *vs.* bond length plot, beginning with the three points having the lowest energy and then expanding by including next neighbour points. This method makes it possible to select a variation range where a parabolic approximation is reasonable. The bond lengths which minimised the total energies were evaluated and adopted as bond lengths for the initial state of the rotation (*P*3 = 0°). To minimise the computational work a mean value of the bond lengths

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[9] D. P. Santry and G. A. Segal, *J. Chem. Phys.*, 1967, **47**, 158.

[10] B. Nelander, *Theor. Chim. Acta*, 1972, **25**, 382.

[11] B. Bak, L. Nygaard, E. J. Pedersen, and J. Rastrup-Andersen, *J. Mol. Spectroscopy*, 1966, **19**, 283.

[12] L. Nygaard, R. L. Hansen, J. T. Nielsen, J. Rastrup-Andersen, G. O. Sörensen, and P. A. Steiner, *J. Mol. Structure*, 1972, **12**, 59.

[13] ' Tables of Interatomic Distances and Configuration in Molecules and Ions,' Chem. Soc. Special Publ. No. 11, London, 1958.

[14] G. Robinet, F. Crasnier, J.-F. Labarre, and C. Leibovici, *Theor. Chim. Acta*, 1972, **25**, 259.

[15] D. H. Christensen, R. N. Kortzeborn, B. Bak, and J. J. Led, *J. Chem. Phys.*, 1970, **53**, 3912.

for compounds (Ia) and (Ie) was calculated and used throughout series (I), and the same procedure was followed in series (II). This procedure is reasonable since, as can be seen in Table 2, the differences in the optimal bond lengths for (Ia) and (Ie) and for (IIa) and (IIe) are very small.

TABLE 2

Exocyclic carbon–nitrogen bond lengths

Compound	Optimal CN distance (Å) Initial state	 Transition state
(Ia)	1·374	1·386
(Ie)	1·384	1·392
(IIa)	1·366	1·384
(IIe)	1·372	1·390
Mean value series (I)	1·379	1·389
Mean value series (II) *sp*	1·369	1·387
Mean value series (II) *spd*	1·378	1·391

The same procedure was employed to determine the bond lengths to be used in the transition state of the rotation ($P3 = 90^\circ$) and the results are summarised in Table 2. It is very satisfactory that this procedure predicts a longer bond for the transition state ($P3 = 90^\circ$) than for the initial state ($P3 = 0^\circ$), as should be expected from the qualitative valence bond description of the two states.

Calculations with a ' Planar ' Dimethylamino-group.—The rotational barriers for compounds (Ia—f) and (IIa—f) have been calculated for $P1 = 120$ and $P2 = 180^\circ$ (the planar model, Figure 1). The barriers are given as the differences between the total energies for $P3 = 90$ and 0°. To investigate the importance of sulphur 3*d*-orbitals on the calculated barriers in compounds (IIa—f), calculations have been made with (*spd* model) and without (*sp* model) 3*d*-orbitals on sulphur. The *sp* and *spd* models used are identical with those described by Santry and Segal.[9] The results are given in Table 3, which also includes the experimental barriers.[7]

TABLE 3

Calculated and experimental barriers. ' Planar ' dimethylamino-group model

Compound	*spd* Model (kJ mol^{-1})	*sp* Model (kJ mol^{-1})	Experimental ($\Delta H^\ddagger$/kJ mol^{-1})
(Ia)		33·5	35·1
(Ib)		30·1	33·9
(Ic)		30·1	31·0
(Id)		31·0	31·0
(Ie)		27·2	<25·5
(If)		25·1	<25·5
(IIa)	50·6	32·2	38·1
(IIb)	45·2	28·0	36·0
(IIc)	46·9	30·5	33·5
(IId)	48·5	29·7	32·6
(IIe)	42·7	26·4	25·9
(IIf)	41·8	25·5	25·5

For one of the compounds, (Ib), the total energy was calculated for several different values of *P*3 using an exocyclic carbon–nitrogen bond length of 1·384 Å (the mean value of the bond lengths for $P3 = 0$ and 90°). The resulting curve is shown in Figure 3. Identical energy maxima are found for $P3 = 90$ and 270°, and minima are found for $P3 = 0$ and 180°. The difference between the energy values for $P3 = 0$ and 180° is negligible. The potential curve shows the validity of using $P3 = 0^\circ$ as initial state and $P3 = 90^\circ$ as transition state for the rotation.

The simple model used in the calculations accounts surprisingly well for the barriers (Table 3). The calculated barriers for compounds (Ia—f) are very close to the experimental ones, while the experimental values for the sulphur compounds (IIa—f) generally lie between those calculated by the two extreme models (the *sp* and *spd* models). A comparison between the calculated and experimental barrier values must be done with caution, considering, for instance, that in these calculations the possibility of different geometries around the amino-nitrogen atom in the initial state and in the transition state has been neglected. A brief study of the effect of pyramidalisation of the dimethylamino-group will be given later in this paper. It should also be noted that the experimental values refer to barriers measured in solution while the calculated barriers correspond to gas-phase values. However, the errors introduced by these simplifications may to a first approximation be considered constant throughout a series of related molecules. The ability of the CNDO/2 method to reproduce experimental substituent effects should be discussed with reference to the 5-unsubstituted compounds (Ie) and (IIe). Unfortunately, the barrier in (Ie) is too low to be measured, but instead a value of 27·2 kJ mol^{-1} has been used, which has been obtained from a least-squares plot of the barriers in (Ia—d) *vs.* the corresponding Hammett σ^- constants. The barrier differences relative to these references are given in Table 4. The general trends of the substituent effects are satisfactorily reproduced by the calculations, but the calculated changes are in general smaller than the experimental ones, which means that the substituent effects are in general underestimated. This may reflect a deficiency of the CNDO/2 method to treat adequately conjugation effects, as has been proposed by Ljunggren and Wettermark[16] and also by Gropen and Seip[17] The cyano-substituted compounds (Ib) and (IIb) show a

TABLE 4

Changes in barriers relative to (Ie) and (IIe)

Compound	*spd* Model (kJ mol^{-1})	*sp* Model (kJ mol^{-1})	Experimental (kJ mol^{-1})
(Ia)		+6·3	+7·9
(Ib)		+2·9	+6·7
(Ic)		+2·9	+3·8
(Id)		+3·8	+3·8
(Ie)		0	0
(If)		−2·1	
(IIa)	+7·9	+5·8	+12·2
(IIb)	+2·5	+1·6	+10·1
(IIc)	+4·2	+4·1	+7·6
(IId)	+5·8	+3·3	+6·7
(IIe)	0	0	0
(IIf)	−0·9	−0·9	−0·4

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[16] S. Ljunggren and G. Wettermark, *Theor. Chim. Acta*, 1970, **19**, 326.

[17] O. Gropen and H. M. Seip, *Chem. Phys. Letters*, 1971, **11**, 445.

particularly serious underestimation of the substituent effect. This is in line with earlier observations, which show that the CNDO/2 approximation somewhat underestimates the electron-withdrawing ability of the cyano-group.[18,19] This underestimation is more serious in the initial than in the transition state and leads to a value for the barrier that is too low.

Effect of 3d-*Orbitals*.—It has been observed that inclusion of 3*d*-orbitals in the basis set of sulphur affects various calculated molecular properties to different degrees. Thus, in calculations on thiophen, Clark [20] has shown that charge densities and the dipole moment are significantly affected by inclusion of 3*d*-orbitals, while the total calculated energy is much less sensitive. However, rotational barriers are generally very small compared to the total energy and small deviations in the stabilising effect of the 3*d*-orbitals between the initial state and the transition state may result in significant changes in the calculated barriers.

Table 3 shows that including 3*d*-orbitals on sulphur increases the barriers by 16—19 kJ mol^{-1}. The calculations on compounds (IIa—f) without 3*d*-orbitals (*sp* model) fail to reproduce the experimental order of the barriers between series (I) and (II). Using the *spd* model, the correct order is obtained, but the differences are exaggerated. The compounds in series (II) have experimental barriers 1·6—3·0 kJ mol^{-1} higher than the corresponding compounds in series (I). The *spd* model gives differences in the range 15·1—17·5 kJ mol^{-1} between the two series.

The addition of 3*d*-orbitals on sulphur stabilises the initial state ($P3 = 0°$) as well as the transition state ($P3 = 90°$). Table 5 gives the differences between the calculated total energies obtained by the *sp* and *spd* models, and shows that the initial states are stabilised by 16—19 kJ mol^{-1} more than the transition states. The increase in the barriers on addition of 3*d*-orbitals to sulphur in compounds (IIa—f) is thus the result of a relatively more stabilised initial state. The exaggerated stabilisation may be a consequence of the too contracted *d*-orbitals obtained by the *spd* model used.[9]

TABLE 5

Differences in total energy between the *sp* and *spd* models

Compound	*P*3 (°)	Difference *sp* — *spd* (kJ mol^{-1})
(IIa)	0	777·8
(IIa)	90	759·4
(IIb)	0	785·8
(IIb)	90	768·6
(IIc)	0	783·7
(IIc)	90	767·3
(IId)	0	784·9
(IId)	90	766·1
(IIe)	0	778·6
(IIe)	90	762·3
(IIf)	0	792·0
(IIf)	90	775·7

Effect of a Pyramidal Dimethylamino-group.—When studying barriers to internal rotation with quantum chemical methods, the choice of structural parameters to be optimised is always a point of discussion. Similar techniques in selecting parameters to be varied, applied to different molecules, may affect the calculated barriers to a varying degree, owing to the properties of the calculation method used.[21]

In this work we have considered geometrical optimisation of the carbon–nitrogen bond, around which the rotation takes place, to be important. An equally important structural parameter, the pyramidality of the dimethylamino-group, will now be discussed. Pyramidal arrangement of the amino-group in aromatic amines is well known from experiments [22,23] and theory.[24]

Compound (Ib) was selected for this study. The exocyclic C–N bond length was kept fixed at 1·384 Å as in Figure 3. The parameters *P*1 and *P*2 (Figure 1) were varied simultaneously and their optimal values were found to within ±5°. This was done for three values of *P*3. The results are given in Table 6. Optimisation leads in all cases to significant stabilisation compared to the planar model (Figure 3). The optimal values for *P*1 and *P*2 for the different values of *P*3 are quite similar. The large deviation from a planar geometry when $P3 = 180°$ is unexpected and casts doubt on the validity of the pyramidalisation procedure. To study this further a common pyramidal situation, $P1 = 107·5$ and $P2 = 117·5°$, was selected and the total energy was

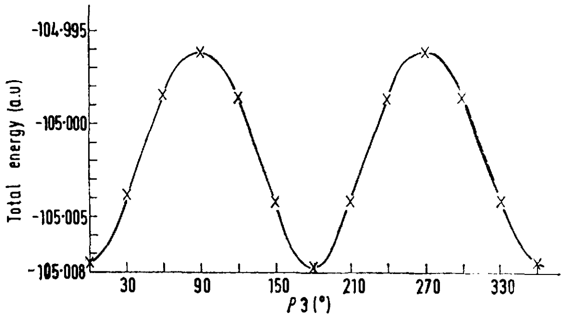

FIGURE 3 Potential curve for the rotation of the dimethylamino-group in (Ib) [$P1 = 120$, $P2 = 180°$, and $R(CN) = 1·384$ Å]

TABLE 6

Optimal pyramidality values

*P*1 (°)	*P*2 (°)	*P*2′ (°)	*P*3 (°)	Stabilisation energy relative to planar form (kJ mol^{-1})
100	115	112·3	90	66·7
105	115	109·1	−90	45·7
110	120	108·9	180	23·1

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[18] R. T. C. Brownlee and R. W. Taft, *J. Amer. Chem. Soc.*, 1970, **92**, 7007.

[19] R. T. C. Brownlee and R. W. Taft, *J. Amer. Chem. Soc.*, 1968, **90**, 6537.

[20] D. T. Clark, *Tetrahedron*, 1968, **24**, 2663.

[21] R. M. Steven, *J. Chem. Phys.*, 1970, **52**, 1397.

[22] D. G. Lister and J. K. Tyler, *Chem. Comm.*, 1966, 152.

[23] J. C. D. Brand, D. R. Williams, and T. J. Cook, *J. Mol. Spectroscopy*, 1966, **20**, 359.

[24] W. J. Hehre, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, 1972, **94**, 1496.

calculated for several values of $P3$. The resulting curve is shown in Figure 4. Not only has the amplitude of the curve decreased compared to the planar case (Figure 3), but the shape of the curve is quite changed, and is now no longer in accord with experiment.[7] The potential curve displays three minima with different energy values. The detailed shape is to some extent an artefact of the fixed staggered conformation of the methyl groups. By allowing them to change freely between the two possible staggered conformations, two minima will obtain the same energy, and the third one will be moved from 75 to 90°. However, the ^1H n.m.r. lineshape should be that of a three-site case where two sites have the same population but the third a different one, and this is in complete disaccord with the experimental results, which show exchange between two equally populated sites.

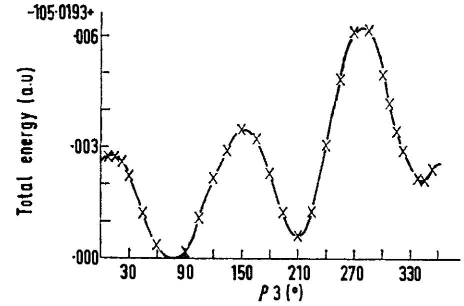

FIGURE 4 Potential curve for the rotation of the dimethylamino-group in (Ib) [$P1 = 107{\cdot}5$, $P2 = 117{\cdot}5°$, and R(CN) = 1·384 Å]

An attempt to analyse the effect of pyramidalisation was made in the following way. With $P1$ fixed at 120°, three potential curves were constructed corresponding to $P2$ = 180, 160, and 140°, and with $P3$ stepped in 30° intervals from 0 to 360°. Two effects are apparent: the total energy decreases, and the energy of the potential maximum at $P3 = 90°$ decreases more rapidly than that at $P3 = 270°$. Figure 5 shows calculated energy values (×) for the case where $P1 = 120$ and $P2 = 140°$.

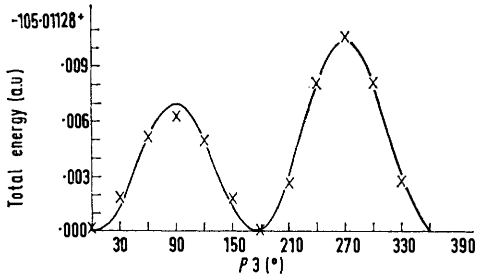

FIGURE 5 CNDO/2 Energy values (×) and Fourier curve (——) for (Ib) as a function of $P3$ ($P1$ = 120, $P2$ = 140°)

An attempt has now been made to resolve the different contributions to the barrier, using the technique of truncated Fourier expansion.[25] The following contributions have been assumed. (*a*) There are non-bonded interactions between the three 'outer' hydrogen atoms [H(1)—(3) in Figure 2(a)] and the oxygen and nitrogen atoms in the ring. These are three one-fold barriers with different phase angles. The latter are calculated from the assumed geometry of the molecule. (*b*) This is an interaction between the lone pair of the dimethylamino-nitrogen atom and the π-orbitals of the ring (*n*–π interaction). This is a two-fold barrier.

These interactions are assumed to be described by cosine functions of the angle $P3 = X$, *e.g.* equation (1) for the interaction between H(2) and N, where ϕ_2 is the phase angle. The expression (2) is obtained for the total

$$V_{\mathrm{NH}} = \tfrac{1}{2}V_{\mathrm{NH}}{}^{\circ}[1 - \cos(X + \phi_2)] \qquad (1)$$

$$V(X) = \tfrac{1}{2}V_{\mathrm{NH}}{}^{\circ}[2 + K_{\mathrm{N}} - K_{\mathrm{N}}\cos(X + \phi_1) - \cos(X + \phi_2) - \cos(X + \phi_3)] + \tfrac{1}{2}V_{\mathrm{OH}}{}^{\circ}[2 + K_{\mathrm{O}} + K_{\mathrm{O}}\cos(X + \phi_1) + \cos(X + \phi_2) + \cos(X + \phi_3)] + \tfrac{1}{2}V_{\mathrm{el}}{}^{\circ}(1 - \cos 2X) \qquad (2)$$

energy. Here $V_{\mathrm{el}}{}^{\circ}$ is the contribution from *n*–π interaction for $X = 90°$, and K_{O} and K_{N} are scaling factors to account for the fact that H(1) is closer to the ring atoms than H(2) and H(3). $V_{\mathrm{NH}}{}^{\circ}$, $V_{\mathrm{OH}}{}^{\circ}$, and $V_{\mathrm{el}}{}^{\circ}$ were obtained by least-squares fitting of curves, calculated by equation (2) for selected pairs of K_{N} and K_{O}, to the appropriate CNDO/2 potential curves. K_{N} and K_{O} were stepped, and the resulting two-dimensional maps were examined for regions of minimum energy. These regions are extremely shallow, but by comparing different maps it was possible to select reasonable values for K_{N} and K_{O}. The fit between the curves calculated by CNDO/2 and expression (2) is quite good, as can be seen in Figure 5 where the case $P1 = 120$ and $P2 = 140°$ is shown. The resulting values for K_{N}, K_{O}, and $V°$ are given in Table 7. From the $V_{\mathrm{el}}{}^{\circ}$ values the following conclusions can be drawn. For $P1 = 120$ and $P2 = 180°$ the *n*–π interaction is of paramount importance for the shape of the potential curve, and the values of K_{N} and K_{O} are without effect. Analysis of the CNDO/2 curves for $P2$ = 160 and 140° shows a gradually diminishing contribution from the *n*–π interaction and an increase in hydrogen–nitrogen and hydrogen–oxygen interaction. The latter appears as an attraction in the pyramidal cases, which is the main reason for the unsymmetrical shape of the potential curves. The decreasing *n*–π interaction with increasing pyramidality of the nitrogen atom is in agreement with the qualitative picture, but the attraction between oxygen and hydrogen

TABLE 7

Coefficients from truncated Fourier expansion

Parameter values		Coefficients found by stepping and least-squares technique				
$P1$ (°)	$P2$ (°)	K_{O}	K_{N}	$10^4V_{\mathrm{OH}}{}^{\circ}$	$10^4V_{\mathrm{NH}}{}^{\circ}$	$10^4V_{\mathrm{el}}{}^{\circ}$
120	180	1·0	1·0	3·6	0·33	110
120	160	2·0	1·7	−14	17	100
120	140	2·0	1·7	−13	15	8·5
110	140	2·0	2·0	−10	11	36
107·5	117·5	2·1	2·1	−2·1	13	7·3

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[25] L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, 1972, **94**, 2371.

also at very short distances is unexpected and alarming. The results suggest that such interactions may increasingly dominate the CNDO/2 picture of the rotation with increasing pyramidality of the dimethylamino-group. Attempts to fit the model function to the case where $P1 = 110$ and $P2 = 140°$ and also for the 'optimal' pyramidal case with $P1 = 107{\cdot}5$ and $P2 = 117{\cdot}5°$ were unsuccessful. It is clear from Figure 6, which shows the case where $P1 = 107{\cdot}5$ and $P2 = 117{\cdot}5°$, that no acceptable approximation could be obtained. It seems that the two maxima emerging in the region $P3 = 0$—$210°$ make an approximation impossible.

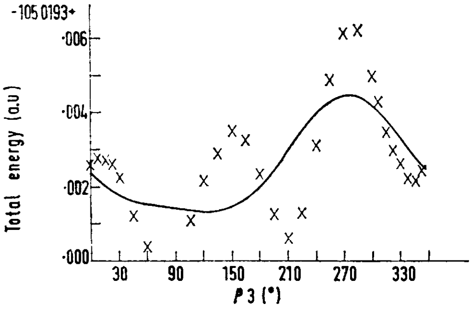

FIGURE 6 CNDO/2 Energy values (×) and Fourier curve (——) for (Ib) as a function of $P3$ ($P1 = 107{\cdot}5$, $P2 = 117{\cdot}5°$)

Working with the hypothesis that our model function is not fundamentally wrong, the above behaviour might be explained if the cosine functions do not simulate non-bonded interactions when the distances are small (down to 2 Å in this case). Perhaps more peaked functions should be used. Attempts to explain the two maxima using simple functions simulating coulomb interactions were also unsuccessful.

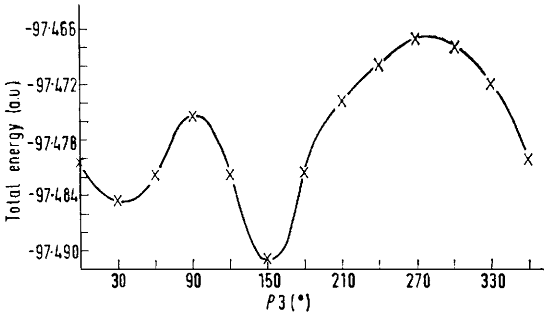

FIGURE 7 Potential curve for the rotation of the dimethylamino-group in (IIb) [$P1 = 107{\cdot}5$, $P2 = 117{\cdot}5°$, R(CN) = 1·378 Å]

To further elucidate the hydrogen–oxygen interactions we calculated the potential curve for the corresponding sulphur compound (Ib) with $P1 = 107{\cdot}5$ and $P2 = 117{\cdot}5°$ using the *spd* model. The result given in Figure 7 shows a more 'normal' curve with at least qualitatively the expected behaviour. Also in this case, however, it was impossible to reproduce the CNDO/2 curve by a function of type (2).

Conclusions.—From the above it is apparent that only the model with a planar nitrogen atom in the dimethylamino-group can reproduce the experimental barriers. With this model, on the other hand, the agreement is remarkably good. When allowance is made for a pyramidal structure of the dimethylamino-group, the agreement breaks down, and in the optimised structure the potential curve is quite unrealistic. A somewhat similar case is found in a CNDO/2 calculation on formamide,[6] for which the planar model gives good numerical agreement with the experimental barrier, but the model with a planar initial state but a pyramidal transition state accounts only for about half the experimental barrier. These results are probably due to a shortcoming of the CNDO/2 method, since at least in the transition state a pyramidal structure seems reasonable.

An analysis of the pyramidal case indicates that the failure is due to an underestimation of the repulsion between non-bonded atoms by the CNDO/2 method. This allows a mutual approach of the methyl groups that is too close and also of the methyl groups and the ring oxygen and nitrogen atoms. The interaction between the oxygen and hydrogen atoms appears as a binding contribution even at the closest approach, at a distance of *ca*. 2 Å. The sum of the van der Waals radii of these atoms is 2·72 Å, and at 2·0 Å a 6–12 Lennard-Jones potential[26] gives a repulsion of 17·6 kJ mol^{-1}. This leads to an incorrect scaling of resonance and steric effects. Dewar and Kohn[27] conclude from calculations on barriers in amides by the MINDO/2 method that only a procedure which explicitly includes one-centre overlap, *e.g*. the NDDO method, can satisfactorily account for barriers where lone pairs are involved. This is substantiated by recent calculations on formic acid by the CNDO/2 and NDDO methods.[28]

We are grateful to the Swedish Natural Science Research Council for financial support and to Dr. B. Nelander for making his CNDO/2 program (*sp* model) available to us.

[2/2709 *Received*, 29*th November*, 1972]

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