

Therefore,

$$P_{00} = 5, P_{20} = (4/27)^{1/2},$$

and the other  $P_{lm}$ 's are zero.

For O atoms, the bonding axis is taken to be  $x(P_1 = 1)$ , and the population of the lone-pair orbitals is assumed to be two ( $P_2 = P_3 = 2$ ) and  $\pi$ -bonding-orbital population  $P_z$  is one, then

$$P_{00} = 6, P_{11+} = -\left(\frac{1}{6}\right)^{1/2}, P_{20} = -(16/243)^{1/2}, \\ P_{22+} = -2/3\pi, P_{11-} = P_{22-} = 0.$$

#### References

- COLAPIETRO, M. & DOMENICANO, A. (1982). *Acta Cryst.* **B38**, 1953–1957.
- COPPENS, P., GURU ROW, T. N., LEUNG, P., STEVENS, E. D., BECKER, P. J. & YANG, Y. W. (1979). *Acta Cryst.* **A35**, 63–72.
- DUNITZ, J. D., SCHWEIZER, W. B. & SEILER, P. (1983). *Helv. Chim. Acta*, **66**, 123–133.
- EYRING, H., WALTER, J. & KIMBALL, G. E. (1944). *Quantum Chemistry*, pp. 223–225. New York: John Wiley.
- FIGGIS, B. N., REYNOLDS, P. A. & WHITE, A. H. (1985). *Inorg. Chem.* **24**, 3762–3770.
- FIGGIS, B. N., REYNOLDS, P. A. & WHITE, A. H. (1987). *J. Chem. Soc. Dalton Trans.* pp. 1737–1745.
- GHELFENSTEIN, M. & SZWARC, H. (1971). *Mol. Cryst. Liq. Cryst.* **14**, 283–288.
- GOPALA KRISHNA, E. M. (1960). *Indian J. Phys.* **34**, 149–151.
- HALL, M. B. (1986). *Chem. Scr.* **26**, 389–394.
- HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
- HANSEN, N. K. & COPPENS, P. (1978). *Acta Cryst.* **A34**, 909–921.
- HIRSHFELD, F. L. (1984). *Acta Cryst.* **B40**, 484–492.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- JENNINGS, L. D. (1984). *Acta Cryst.* **A40**, 12–16.
- KUJIMA, N., TANAKA, K. & MARUMO, F. (1981). *Acta Cryst.* **B37**, 545–548.
- KUJIMA, N., TANAKA, K. & MARUMO, F. (1983). *Acta Cryst.* **B39**, 557–561.
- KIKKAWA, T., OHBA, S., SAITO, Y., KAMATA, S. & IWATA, S. (1987). *Acta Cryst.* **B43**, 83–85.
- MASLEN, E. N. & SPADACCINI, N. (1989). *Acta Cryst.* **B45**, 45–52.
- MILLER, R. S., PAUL, I. C. & CURTIN, D. Y. (1974). *J. Am. Chem. Soc.* **96**, 6334–6339.
- MIYATA, N., TANAKA, K. & MARUMO, F. (1983). *Acta Cryst.* **B39**, 561–564.
- OHBA, S., SHIOKAWA, K. & SAITO, Y. (1987). *Acta Cryst.* **C43**, 189–191.
- PLoug-Sørensen, G. & Andersen, E. K. (1985). *Acta Cryst.* **C41**, 613–615.
- RAE, A. D. (1978). *Acta Cryst.* **A34**, 719–724.
- SCHWARZ, W. H. E., VALTANOS, P. & RUEDENBERG, K. (1985). *Theor. Chim. Acta*, **68**, 471–506.
- SEILER, P., SCHWEIZER, W. B. & DUNITZ, J. D. (1984). *Acta Cryst.* **B40**, 319–327.
- SPACKMAN, M. A. & MASLEN, E. N. (1985). *Acta Cryst.* **A41**, 347–353.
- STEVENS, E. D. & COPPENS, P. (1979). *Acta Cryst.* **A35**, 536–539.
- TAKAZAWA, H., OHBA, S. & SAITO, Y. (1988). *Acta Cryst.* **B44**, 580–585.
- TANAKA, K. & MARUMO, F. (1983). *Acta Cryst.* **A39**, 631–641.
- TROTTER, J., WHITLOW, S. H. & ZOBEL, T. (1966). *J. Chem. Soc. A*, pp. 353–356.
- WHEELER, G. L. & COLSON, S. D. (1975). *J. Chem. Phys.* **65**, 1227–1235.
- ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

*Acta Cryst.* (1989). **B45**, 437–442

## Investigation of the Intermolecular Potential Hypersurface of *N,N*-Dimethyl-*p*-nitroaniline

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#### Abstract

Atom–atom potentials are used to calculate the lattice energy of *N,N*-dimethyl-*p*-nitroaniline for a selection of space-group symmetries. The aim is to demonstrate the viability of computer models to select crystal forms of interest in nonlinear optical applications.

#### Introduction

The critical problem of designing new molecules to produce crystals with large second-order susceptibilities

is the indeterminacy of their crystal form. If synthetic effort is to be used efficiently then it is important to include in the initial design as much information as possible on the factors influencing the crystalline form of the proposed molecule.

This study investigates the applicability of a semi-empirical atom–atom potential, as a representation of the intermolecular interaction, to the problem of determining influences on the selected molecular arrangement.

The molecule *N,N*-dimethyl-*p*-nitroaniline (DIM-NAN) (Mak & Trotter, 1965) satisfies the requirements for producing a high first hyperpolarizability,  $\beta$ , and was chosen as representative of a large class of substituted benzene molecules examined by various

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groups throughout the world for their nonlinear optical properties (Chemla & Zyss, 1987). From the point of view of this study, it has the important feature of a dimethylamino group instead of a simple amine donor. This not only increases the magnitude of the hyperpolarizability (Morley, Docherty & Pugh, 1987) but removes the problem of modelling the hydrogen-bonding interaction between the nitro and amine groups of adjacent molecules found, for example, in *p*-nitroaniline (Colapietro, Domenicano, Marciante & Portalone, 1982). Several closely related molecules have already demonstrated their potential to produce crystals with large second-order susceptibilities (Chemla & Zyss, 1987). The critical difference between the systems is their crystalline form. For any sizeable effect to be produced the molecules of a crystal must avoid an antiparallel alignment of the charge-transfer axes. DIMNAN is a good example of the problem group of pseudo-centrosymmetrical materials.

### Methodology

All the calculations reported below use the program PCK83 (Williams, 1982). In this routine a Buckingham potential is used to represent the intermolecular interaction, namely:

$$U_{IJ} = -A_{IJ}/R_{IJ}^6 + B_{IJ}\exp(-C_{IJ}R_{IJ}) + KQ_I Q_J / R_{IJ}^n \quad (1)$$

where the three terms are taken to represent the dispersive, repulsive and electrostatic interactions, respectively. The parameters in the above equation were obtained by Williams *et al.* (Williams & Starr, 1977; Cox, Hsu & Williams, 1981; Williams & Cox, 1984) from a least-squares fitting to known selected structures and energies. The parameters are therefore optimized to compensate within the limits of the chosen functional form for the inadequacies of the representation. There are a number of well-recognized problems associated with the simple representation given by (1). The attractive dispersion force represented above by the  $R^{-6}$  dependence is based on analogy with the approximate London interaction between spherical atoms, while the exponential term models the charge overlap and exchange repulsions. Higher order and anisotropic interaction contributions are subsumed into the  $A$  and  $B$  parameters, while the  $C$  parameter is set independently due to the difficulties of including it in the least-squares refinement.

A more-highly developed semi-empirical potential could be used, which has a more complex description of the dispersion energy and includes induction and other contributions, but except for a term representing the hydrogen-bonding interaction in an appropriate case, this extension cannot currently be justified. The extension of the potential would introduce a large number of extra parameters, the values of which would be difficult to estimate.

The theoretical problem of relating intermolecular interactions to a sum of interactions between local groups on the interacting molecules has yet to be solved (Claverie, 1976). There is therefore no consistent hierarchy of approximate potential forms currently available. This problem does not exist for the electrostatic interaction for which numerous approximation schemes are available (Stone & Alderton, 1985; Goldblum, Perahia & Pullman, 1979), although these become increasingly difficult to implement as the size of the system increases. The complexity of the representation is also limited by the requirements of the convergence acceleration technique, which is very important in achieving fast and reliable summations (Williams, 1972). Currently, the method cannot cope with a dipole-monopole or dipole-dipole interaction potential in a polar space group. In this particular case the site charges  $Q_i$  for the monopole representation used are obtained from the molecular wavefunction using a least-squares fitting technique (Cox & Williams, 1981).

Williams produces a thermally averaged set of parameters by using structural data obtained at varying temperatures, without adjustment, and equating the internal energy of particular members of the data set to their measured heat of sublimation, corrected to zero K. The conventional approximate relationship between the sought-after internal energy and the measured enthalpy (Mirsky, 1976):

$$H_{\text{sub}} = U - 2RT, \quad (2)$$

therefore does not apply and the terms are more appropriately equated.

### Results

#### Observed structure

The first step in the investigation was the examination of the observed crystalline form, to see if this could be satisfactorily reproduced using an atom-atom potential approximation with standard parameter values.

The H-atom locations were not fully refined in the X-ray determination of the monoclinic  $P2_1$  structure of DIMNAN (Mak & Trotter, 1965) and were therefore added using molecular graphics at  $sp^2$  and  $sp^3$  orientations, as appropriate, with bond lengths of 1.08 and 1.09 Å, respectively. An *ab initio* quantum-mechanical calculation at the STO-3G level of approximation was then carried out to provide the wavefunction and hence the electrostatic potential. The point charges produced by least-squares fitting to the calculated electrostatic potential were increased by a factor of 1.13 in line with the results of comparative calculations on small molecules at STO-3G and 6-31G\*\* levels (Cox & Williams, 1981). The C-H

bond lengths were then shortened by 0.07 Å to account for the displacement of the electron density into the bond and because it was on this basis that the van der Waals parameters were derived (Williams, 1981).

The STO-3G calculations provided a Mulliken population-analysis estimate of the dipole moment of 7.02 debye ( $23.4 \times 10^{-30}$  C m) but the point-charge model used in the packing calculations reported below gave an effective dipole moment of 8.01 debye ( $26.7 \times 10^{-30}$  C m).

As shown in Fig. 1 the observed arrangement is well reproduced by the calculated structure obtained from submitting the asymmetric unit to the crystal-packing program PCK83. The molecular translation along the twofold axis is redundant thus reducing to nine the number of independent variables involved in the energy minimization. The main differences between the observed and calculated unit cells are displayed in Table 1.

The average parameters and simple potential representation adopted in the Williams program clearly cannot be expected to give a completely accurate reproduction of a particular crystal form. The good agreement found for DIMNAN is therefore encouraging and extends to the predicted lattice energy. Although from the comments above incapable of high accuracy, it is in reasonable agreement with the heat of sublimation, an experimental quantity which is correspondingly difficult to measure.

The heat of sublimation has been measured within ICI and by Majury (Majury, 1956) using the vapour-pressure technique. The results are consistent and give respectively:

$$H_{\text{sub}} = 110 \pm 4 \text{ kJ mol}^{-1} \text{ at } 298 \text{ K,}$$

$$H_{\text{sub}} = 98.7 \pm 1.7 \text{ kJ mol}^{-1} \text{ at } 344\text{--}366 \text{ K.}$$

This is in excellent agreement with the calculated value reported in Table 2.

Modifications were made to the model in particular how the charge is represented, by, for example,

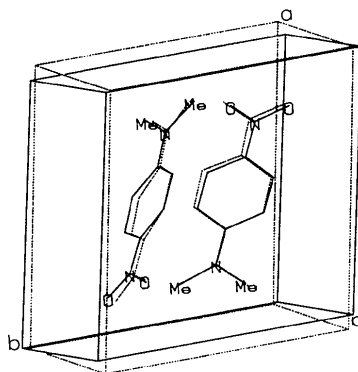


Fig. 1. Observed and calculated unit cells of DIMNAN superimposed. The calculated structure was started from the experimentally observed parameter settings and is shown by the solid lines.

Table 1. Comparison of the observed and calculated unit cells of DIMNAN

	Observed ( $x^\circ$ )	Calculated ( $x$ )	Deviation ( $x-x^\circ$ )/ $x^\circ$
<i>a</i>	9.73 (1) Å	9.25 Å	-4.9%
<i>b</i>	10.56 (1) Å	11.09 Å	5.0%
<i>c</i>	3.964 (5) Å	3.998 Å	0.86%
$\beta$	91.47 (8)°	83.70°	-8.5%
<i>V</i>	407.2 Å <sup>3</sup>	407.65 Å <sup>3</sup>	0.1%

Table 2. Results for DIMNAN

Observed structure  $P2_1$ , volume = 407 Å<sup>3</sup>

Form	Energy (kJ mol <sup>-1</sup> )	Model	Volume (Å <sup>3</sup> )
$P\bar{1}$	-100.13	PD-STO-3GN-FS	410
$P\bar{1}_{\text{ROT}}$	-100.57	PD-STO-3GN-FS	405
$P2_1$	-100.54	PD-STO-3GN-FS	408
$P2_1^{\text{RP}}$	-100.55	PD-STO-3GN-FS	408
$P2_1^{\text{ROT}}$	-99.42	PD-STO-3GN-FS	408
$P2_1^{\text{UC}}$	-201.07	PD-STO-3GN-FS	408
$P2_1$	-101.24	PD-FS-STO-3GN	408
$P2_1$	-100.33	PD-STO-3GN-FS-LP	408
<i>Cc</i>	-83.48	PD-STO-3GN-FS	891
$P2_1/c$	-94.53	PD-STO-3GN-FS	820
<i>C2/c</i>	-93.60	PD-STO-3GN-FS	1728
$P2_12_12_1$	-93.61	PD-STO-3GN-FS	840
<i>Pbca</i>	-89.70	PD-STO-3GN-FS	1718

Notes: PD indicates potential-derived charges least-squares fitted to the electrostatic potential calculated directly from the molecular wavefunction. STO-3G indicates the quantum-mechanical level of approximation used in the charge calculation. N indicates that the charges have been rescaled by a factor of 1.13. This is an approximate factor relating results calculated at the STO-3G level of approximation with corresponding results at the 6-31G\*\* level (Cox & Williams, 1981). FS indicates that the C-H bond lengths have been foreshortened by 0.07 Å (Williams, 1981). If this is placed immediately after the PD symbol it indicates that the charges were calculated at the foreshortened positions instead of placed there after calculation at the standard bond lengths used in the wavefunction. This would be the correct procedure if the wavefunction demonstrated foreshortening. LP indicates that lone pairs have been introduced at 0.25 Å from the O atoms in an  $sp^2$  configuration to improve the charge representation. UC indicates that all the molecules of the unit cell are treated independently and only translational symmetry is applied ( $P1$ ). The energy per molecule is given by dividing by the number of molecules per unit cell. RP indicates that a non-experimentally observed starting position has been employed in a calculation of the experimentally observed form. ROT indicates that the methyl groups have been rotated by 60° and the calculation repeated from the previous minimized position.

introducing lone pairs on the O atoms, to see if an improved, or at least alternative, representation would result in the calculated structure being more tightly bound. Although a difference was observed, it is probably too small to be considered significant.

Another modification (Table 2) to the standard approach was the calculation of the experimentally observed  $P2_1$  structure while assuming both molecules in the unit cell to be independent and thus only applying translational symmetry. The positional degeneracy along the twofold axis was not lifted by the removal of point-group constraints and, although not affecting the calculated energy, structural convergence could only be achieved by stopping translation along the twofold axis.

#### Postulated structures

Highly populated space groups (Mighell, Himes & Rodgers, 1983) were selected as trial symmetries for lattice-energy minimizations of DIMNAN, with the

molecule constrained to be rigid. This approximation is justified by the through conjugation of the molecule, which makes any large conformational change exact a large energy penalty. Thus, any calculated lattice energy of a nonobserved, hypothetical polymorph should be considered an upper bound and hence an under estimate of how well packed the structure might be, owing to the possibility of the molecule relaxing into the optimum conformation for that symmetry.

The calculation procedure necessarily involved repeated minimizations in each of the selected space groups, in an attempt to overcome the problem of subminima. There is of course no guarantee of success with this procedure and the calculated energies again represent an upper bound.

The energies found for the material in the various arrangements are closely spaced as shown in Table 2. This lends credence to the quality of the minima found since they come close to the energy of the observed structure after relaxation, but it imposes a need to rely on a high relative accuracy for the calculations, even if the absolute scaling is in error. Support for the relative accuracy of the atom-atom potential method in comparing different packing energies is given in the short discussion on the topic by Pertsin & Kitaigorodsky (1987).

The most interesting result is that for the centrosymmetric triclinic form. As shown in Figs. 1 and 2, the two crystal arrangements are very similar and it is therefore reasonable that their energies should be close. The energies calculated are, however, sufficiently close that there is a reasonable expectation, based on this result, that the molecule should be polymorphic. The free volume available to the molecules is different in each case; the triclinic form is more loosely packed but neither system appears to show any significant clash, even if the methyl groups are rotated.

Test calculations carried out with rotated methyl groups do, however, shed light on the nonobservance of the triclinic form when the molecule is recrystallized from a variety of solvents (Mclean, 1987). This

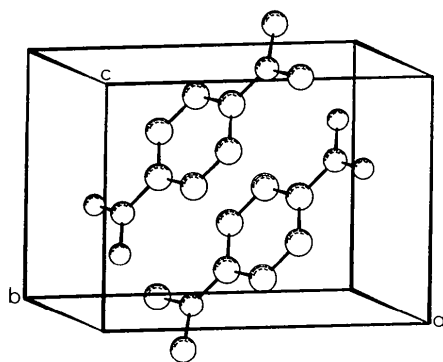


Fig. 2. Ball-and-stick representation of the calculated  $P1$  structure of DIMNAN. O atoms can be identified as the smaller spheres.

assumes that the nonappearance of the modification is substantive, *i.e.*, that an alternative approach would not succeed in finding the polymorphic modification and that the simple recourse of rejecting the model calculations as inadequate is premature. Intramolecular interactions are not considered in the calculations reported below, where the crystal structure is calculated with staggered methyl groups. This form, with the methyl groups rotated by  $60^\circ$  from the assumed eclipsed orientation, can be regarded as a transition state for a rotation under the threefold symmetry of the potential. A recent analysis (Cavagnat & Pesquer, 1986) of the rotation of the methyl group in a crystal of nitromethane at low temperatures (4 K) has identified the terms in the rotation potential with the intermolecular interaction of neighbouring groups. The case of DIMNAN will be much more difficult to analyse because of the increased role of the intramolecular interactions but must await more experimental data. There is no direct experimental evidence available on the rotational motion of the methyl groups in DIMNAN but the authors of the structural determination did comment on the large torsional motions of both the N—Me and N—O bonds.

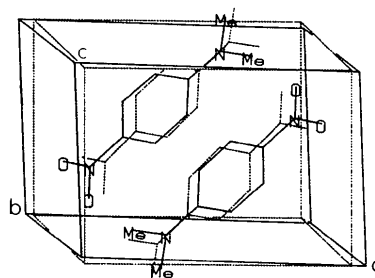


Fig. 3.  $P1$  form of DIMNAN calculated with and without a methyl-group rotation of  $60^\circ$ . The methyl-rotated structure is shown by the solid lines and demonstrates the significant change in the position of the molecules and the size of the unit cell as a result of the rotation.

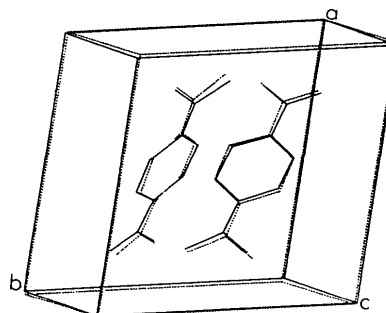


Fig. 4.  $P2_1$  form of DIMNAN calculated with and without a methyl-group rotation of  $60^\circ$ . The methyl-rotated structure is shown by the solid lines and demonstrates a negligible change in the position of the molecules and the size of the unit cell as a result of the rotation.

Table 3. *Initial and final energies (kJ mol<sup>-1</sup>)*

Space group	Initial energy	Final energy
$P\bar{1}$	-85.79	-100.13
$P2_1$	-95.50	-99.42

Notes: initial energy is the energy calculated for the molecule with rotated methyl groups when constrained to have the same position, orientation and unit cell as the calculated standard form. Final energy is the energy achieved when the position, orientation and unit-cell parameters are allowed to relax into a new arrangement suitable for a molecule with rotated methyl groups.

The calculations show a negligible change in the packing energy, but significant movement in the location of the molecule and the size of the unit cell for the triclinic arrangement. The monoclinic form, however, shows negligible changes in all parameters when minimized with rotated methyl groups (see Figs. 3 and 4). Table 3 demonstrates that the initial energy of the methyl-rotated triclinic system before being allowed to relax into its displaced position is much less favourable than the corresponding unrelaxed monoclinic system. This would suggest a greater stability, when the rotations are not locked in phase, for the experimentally observed form where the intermolecular contribution to the methyl-group rotation barrier is less than in the triclinic case. This supports the conjecture that, because methyl groups will be rotating rapidly in solution, the crystal form which is stable to such perturbations will have an advantage and thus more readily coalesce out.

At this stage an important development was introduced into the experimental symmetry comparison. The energy minimization of the observed form was repeated on the same basis as the rest of the hypothetical symmetry calculations. This involved starting with a nonobserved asymmetric unit orientation, with the unit cell initially taken as cubic and of side 10 Å. The initial orientation was taken to be that of the asymmetric unit in the  $P2_12_12_1$  orthorhombic form (see Fig. 5). The result of this calculation is in excellent agreement with the previously calculated result, as displayed in Fig. 6.

### Concluding remarks

Molecules with more than one kind of hetero atom were not included in the set used to derive the atom-atom parameters and it was not known how well the parameters would perform, particularly since the molecule under study was strongly polar. The results reported for this material are satisfactory but new molecules appropriate to nonlinear optics must be tried, particularly polymorphic ones, since this will help to resolve the question of whether the technique can be used to screen for candidate materials (Higgins, 1989).

The essential problem of applying the method of atom-atom potentials to the modelling of crystal form is not the adequacy of the potential in terms of how well it represents the true intermolecular interaction. The

true interaction and the associated parameters are in any event insufficiently well determined for a comparison. The evidence suggests that the empirical potential models the interaction remarkably well given the correct molecular form. The overriding problems are those of minor conformational change and sub-minima in the potential-energy surface.

The first problem can be tackled with increased computational effort by introducing molecular mechanics to adjust the conformation, or, if the computing resources are available, a quantum-mechanical calculation of the conformation subject to the constraints of the intermolecular potential. Fortunately, the particular problem of nonlinear optical crystals is more susceptible to solution than the general case because of the rigidity required of the molecules. The second problem is more difficult to overcome since there is no quick method of finding the global minimum. A practical procedure will require the introduction of sampling into the model, so that several energy minima

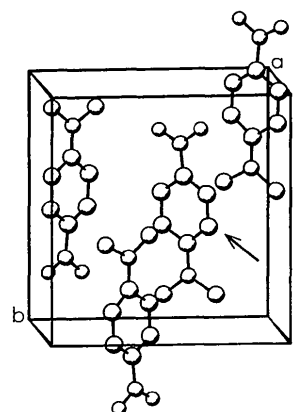


Fig. 5. Ball-and-stick representation of the calculated  $P2_12_12_1$  structure of DIMNAN with the asymmetric unit used in Fig. 6 shown by the arrow. O atoms can be identified as the smaller spheres.

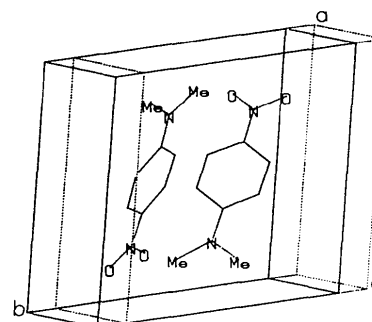


Fig. 6. Two  $P2_1$  unit cells of DIMNAN superimposed, with one the calculated unit cell of Fig. 1 (solid line) and the other (broken line) calculated from the asymmetric unit orientation shown in Fig. 5. The molecular structures completely overlap in the figure.

are picked and subjected to a Bayesian test (Boender & Kan, 1987), or if a deterministic solution is required, the use of interval analysis (Hansen, 1980). This latter option, although desirable, is not critical since substantial benefit could be accrued by reducing the number of molecules that are synthesized and found to be ineffective without attempting to eliminate entirely, within the confines of the model, the possibility of redundant effort.

The important conclusion to be drawn is that two very similar arrangements ( $P_1$  and  $P_2$ ) were selected from nonobserved starting positions and that if they had been taken as indicating whether synthesis should be carried out the material would, correctly, not have been produced.

This is the first step in developing a screening procedure capable of selecting candidate molecules for synthesis.

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#### References

- BOENDER, C. G. E. & KAN, A. H. G. R. (1987). *Math. Program.* **37**, 59–80.
- CAVAGNAT, D. & PESQUER, M. (1986). *J. Phys. Chem.* **90**, 3289–3293.
- CHEMLA, D. S. & ZYSS, J. (1987). Editors. *Nonlinear Optical Properties of Organic Molecules and Crystals*, Vol. 1. New York: Academic Press.
- CLAVERIE, P. (1976). *Localization and Delocalization in Quantum Chemistry*, Vol. 2, edited by D. CHALVET, R. DAUDEL & S. DINER, pp. 127–152. Dordrecht: D. Reidel.
- COLAPIETRO, M., DOMENICANO, A., MARCIANTE, C. & PORTALONE, G. (1982). *Z. Naturforsch.* **37**, 1309–1311.
- COX, S. R., HSU, L. Y. & WILLIAMS, D. E. (1981). *Acta Cryst.* **A37**, 293–301.
- COX, S. R. & WILLIAMS, D. E. (1981). *J. Comput. Chem.* **2**, 304–323.
- GOLDBLUM, H., PERAHIA, D. & PULLMAN, A. (1979). *Int. J. Quantum Chem.* **15**, 121–129.
- HANSEN, E. (1980). *Numer. Math.* **34**, 247–270.
- HIGGINS, N. A. (1989). *Acta Cryst.* **B45**, 442–447.
- MCLEAN, T. D. (1987). Private communication.
- MAJURY, T. G. (1956). *Chem. Ind.* pp. 349–350.
- MAK, T. C. W. & TROTTER, J. (1965). *Acta Cryst.* **18**, 68–74.
- MIGHELL, A. D., HIMES, V. L. & RODGERS, J. R. (1983). *Acta Cryst.* **A39**, 737–740.
- MIRSKY, K. (1976). *Acta Cryst.* **A32**, 199–207.
- MORLEY, J. O., DOCHERTY, V. J. & PUGH, D. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. 1357–1360.
- PERTSIN, A. J. & KITAIGORODSKY, A. I. (1987). *The Atom-Atom Potential Method*, Springer Series in Chemical Physics Vol. 43. Berlin: Springer-Verlag.
- STONE, A. J. & ALDERTON, M. (1985). *Mol. Phys.* **56**, 1047–1064.
- WILLIAMS, D. E. (1972). *Acta Cryst.* **A27**, 452–455.
- WILLIAMS, D. E. (1981). *Topics in Current Physics*, Vol. 26, *Crystal Cohesion and Conformational Energies*, edited by R. M. METZGER, pp. 3–40. Berlin: Springer-Verlag.
- WILLIAMS, D. E. (1982). PCK83. Quantum Chemistry Program Exchange No. 481.
- WILLIAMS, D. E. & COX, S. R. (1984). *Acta Cryst.* **B40**, 404–417.
- WILLIAMS, D. E. & STARR, T. L. (1977). *Comput. Chem.* **1**, 173–177.

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## Theoretical Study of Polymorphism in (*E*)-2-Dimethylamino-1-(5-nitro-2-furyl)ethylene

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#### Abstract

Lattice-energy calculations for polymorphic crystal modifications of (*E*)-2-dimethylamino-1-(5-nitro-2-furyl)ethylene are reported. The results demonstrate the information that can be gained from this type of calculation and its potential to provide a qualitative screening tool for the crystal forms of the organic molecules appropriate for  $\chi^{(2)}$  applications.

#### Introduction

An investigation of the intermolecular potential-energy variation, calculated by the atom-atom summation technique (Williams, 1981), for the experimentally determined molecular conformations of a polymorphic crystal under both experimentally observed and hypothetical symmetry constraints is reported. The results and approach have application to the search for new organic second-order nonlinear optical materials.

Estimates can be made of the first hyperpolarizability,  $\beta$  (Morley, Docherty & Pugh, 1987),

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