

Dimethyl (Dimethylaminomethylene)malonate: Crystal Structure and Dynamic Behaviour in Solution

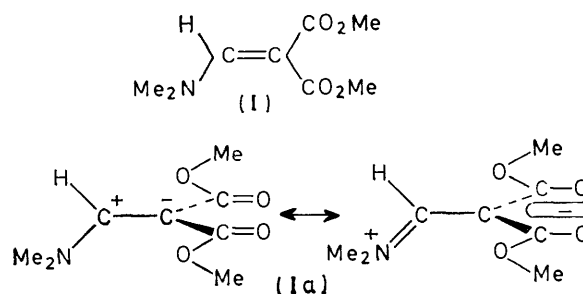
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The structure of the title compound (I) was determined from photographic X-ray data. Crystals are monoclinic, space group $P2_1/a$, with $Z = 4$ in a unit cell of dimensions: $a = 6.200 \pm 0.002$, $b = 12.144 \pm 0.002$, $c = 12.859 \pm 0.002$ Å, and $\beta = 86.41 \pm 0.04^\circ$. The structure was solved by direct methods and refined by full-matrix least-squares techniques to $R = 0.055$ for 867 observed reflections.

The molecule consists of two essentially planar parts: the *trans*-dimethylaminoacrylate portion, and the remaining methoxycarbonyl group. The nitrogen atom is coplanar with its bonded neighbours. The bond lengths of the group N=C are N-C 1.337 and C=C, 1.380 Å, indicating extensive delocalisation. Comparison with i.r. results suggests a similarity of the conformations of (I) in the crystalline and liquid phases, and enables the ΔG^\ddagger value for isomerisation about the C=C bond in the similarly delocalised methyl *trans*-3-dimethylaminoacrylate to be estimated as 30.8 kcal mol⁻¹. The lower value for (I), 15.6 kcal mol⁻¹, cannot be ascribed to its ground-state delocalisation and should be attributed mainly to a stabilisation of the dipolar transition-state.

DIMETHYL (DIMETHYLAMINOMETHYLENE)MALONATE (I) and compounds of related structure have been extensively investigated by use of n.m.r. spectroscopy.¹⁻³ It was found that (I) undergoes two unimolecular kinetic processes with rates which are within the n.m.r. time scale.¹ The first is isomerisation about the C=C (formal) double-bond with free energy of activation of 15.6 kcal mol⁻¹ at 18.5 °C in CH₂Cl₂. The second process is associated with the rotation about the N-C (formal) single-bond with free energy of activation of 13.3 kcal mol⁻¹ at -9.0 °C in CH₂Cl₂. These kinetic processes were investigated by studying the changes in the n.m.r. line-shape with temperature of the two diastereotopic methoxycarbonyl groups and dimethyl amino-groups. Similar studies were carried out with sundry compounds, varying the electronic nature of the double-bond substituents.¹⁻³ The striking property of compound (I) and its related derivatives is the low magnitude of the barrier to isomerisation about the carbon-carbon double bond. Thus, it was found that dimethyl (1-dimethylaminoethylidene)malonate isomerises at a rate which is outside the n.m.r. time scale, and the energy barrier (ΔG^\ddagger) was estimated at ca. 6.2 kcal mol⁻¹.¹ This strikingly low value is well within the range of barriers for rotation about carbon-carbon single-bonds. We wished to know to what extent the structure of the double bond is preserved in such a compound, considering that the localised double bond of ethylene (CHD:CHD) requires 61 kcal mol⁻¹ for isomerisation.⁴ The rate of isomerisation is a function of both the structure of the ground state of the molecule and its transition state in the isomerisation process. The experimental evidence at present available¹ allows us to describe the transition state by the dipolar specie (Ia). Electron delocalisation effects in the ground state are expected to accelerate the isomerisation inasmuch as less energy will be required to overcome the π bonding in proceeding to the transition

state. However, those same functional groups which, in the ground state, accelerate the isomerisation process will also operate to stabilise the transition state for the same process, *i.e.* the malonate moiety, which, in the



ground state induces electron delocalisation will also stabilise the developed negative charge in the transition state (Ia). Since the electronic effects in the ground and the transition states are operating in the same direction, *i.e.*, lowering the energy barrier, it is difficult to assess their relative contribution to the rate of isomerisation. It has been calculated⁵ that π bond orders are 0.75–0.85 for similarly delocalised configurationally unstable olefins, suggesting that the double-bond character in this type of compound is essentially preserved. We have therefore undertaken an X-ray structure analysis of (I) in order to clarify this problem and to determine the conformational details of the molecule. Specifically, it was desired to determine the magnitude of the expected electron delocalisation and evaluate its importance in the unusually fast isomerisation process. It is believed that the main structural features of (I) can be related to similar systems, and consequently their kinetic behaviour could be better understood.

¹ Y. Shvo and H. Shanan-Atidi, *J. Amer. Chem. Soc.*, 1969, **91**, 6683.

² Y. Shvo and H. Shanan-Atidi, *J. Amer. Chem. Soc.*, 1969, **91**, 6689.

³ Y. Shvo and I. Belsky, *Tetrahedron*, 1969, **25**, 4649.

⁴ B. S. Rabinovitch, J. E. Douglas and F. S. Looney, *J. Chem. Phys.*, 1952, **20**, 1807; 1955, **23**, 315.

⁵ J. Sandström and I. Wennerbeck, *Acta Chem. Scand.*, 1970, **24**, 1191.

EXPERIMENTAL

Crystal Data.— $C_8H_{13}NO_4$, $M = 187.2$. Monoclinic, $a = 6.200(2)$, $b = 12.144(2)$, $c = 12.859(2)$ Å, $\beta = 86.41(4)^\circ$, $U = 966.4$ Å³, $D_m = 1.29$ (by flotation), $Z = 4$, $D_c = 1.286$. Weissenberg photographs, Cu- K_α radiation: $\lambda(Cu-K_{\alpha 1}) = 1.5405$, $\lambda(Cu-K_{\alpha 2}) = 1.5443$ Å; and precession photographs Mo- K_α radiation: $\lambda(Mo-K_\alpha) = 0.7107$ Å; $\mu(Mo-K_\alpha) = 1.1$ cm⁻¹. Space group $P2_1/a$.

Cell data were derived from their least-squares fit to 57 observations. Intensity data were collected from microdensitometer measurements of integrated precession photographs, by use of a Nonius-Enraf precession camera and a Joyce-Loebl III CS recording microdensitometer. Intensities of 2368 reflections were obtained from the layers $h0-5l$ and $hk0-5$ and were reduced to structure amplitudes in the usual manner. No absorption corrections were applied. 222 Non-zero reflections, common to different layers, served to place the data on a common scale. 2002 Independent reflections including 873 reflections with intensities $1/3I_{min}$ were collected. Each reflection was assigned a weighting parameter, depending on the estimated accuracy of the microdensitometer readings of its intensity, which was later incorporated into the weighting scheme employed in the refinement of the structure.

Approximate scale- and temperature-factors were obtained by Wilson's⁶ method and were used in the calculation of normalised structure amplitudes. The experimental means of some functions of $|E|$ and the distribution of the $|E|$ values among the data are compared with the corresponding theoretical values in Table 1.

TABLE 1

Some functions of $|E|$ and the % distribution of their magnitudes

	Found	Calc. (centrosymm.)
$\langle E ^2 \rangle$	0.998	1.0
$\langle E \rangle$	0.820	0.798
$\langle E ^2 - 1 \rangle$	0.945	0.968
$ E > 3$	0.4%	0.3%
$ E > 2$	4.5%	5.0%
$ E > 1$	28.9%	32.0%

Computations were carried out on CDC 3400 and 6600 computers at the Tel-Aviv University Computation Centre with programs most of which have been described elsewhere.^{7,8}

Determination of the Structure.—The starting set of signs (Table 2) was obtained with the aid of a modified version of the DIRECT 1 programme,⁸ and was used with the multisolution routine of Long,⁹ to yield sixteen sets of signs for the 203 $|E|$ values ($|E| > 1.60$) employed. One of the sets had a consistency index⁹ (C 0.84) much higher than the others and was obtained in only two iteration cycles. Apart from these two acceptance criteria being satisfied by this set, it also confirmed the signs indicated for three structure invariants [$E(002) - 2.18$, $E(008) + 2.53$, and $E(60\bar{1}2) - 2.19$] by the Σ_1 relationship.¹⁰ All the non-hydrogen

† For details see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20.

⁶ A. J. C. Wilson, *Nature*, 1942, **150**, 152.

⁷ I. Goldberg and U. Shmueli, *Acta Cryst.*, 1971, **B**, **27**, 2164.

⁸ I. Goldberg and U. Shmueli, *Acta Cryst.*, 1971, **B**, **27**, 2173.

⁹ R. Long, Ph.D. Thesis, 1965, University of California, Los Angeles.

atoms of (I) were located in an E map based on the above solution. The trial structure so obtained readily refined isotropically to R 0.16 leading to acceptable interatomic distances and confirming the correct indication of all the signs by Long's routine.⁹ No further sign changes of these reflections were observed in subsequent calculations.

TABLE 2

Starting set of signs

h	k	l	E	N^*	
1	2	$\bar{2}$	+2.96	52	} Origin-fixing
3	9	2	+3.37	47	
3	5	$\bar{7}$	+3.03	41	
1	6	$\bar{1}$	2.89	37	} Signs permuted
4	3	$\bar{6}$	2.79	38	
6	3	$\bar{7}$	3.41	36	
4	8	5	3.37	27	

* N is the frequency of occurrence in high-probability triple products.

The weighting function employed in the least-squares refinement is given by $w = [aK^2 + (bF_o^2/4w_o)]^{-1}$ where K is the scale factor and w_o is the experimental weighting parameter, defined as $w_o(I) = I^2/\sigma^2(I) = F_o^4/\sigma^2(F_o^2)$ assigned to each reflection during processing of the data. The values of the constants were a 1 and b 0 in isotropic refinement rounds and a 0, b 1 in all subsequent calculations.

Full-matrix refinement, based on all the observed reflections, of the positional and anisotropic thermal parameters of the heavy atoms reduced R to 0.090. At this stage, four sections of difference-Fourier were computed and enabled the methyl hydrogen atoms to be located. The vinylic hydrogen, H(26), was inserted at its expected location. The positional parameters of the thirteen hydrogen atoms were kept in a separate block while their thermal parameters were held fixed at $u_H = 0.06$ Å² during subsequent calculations. These were concluded with a few cycles of refinement which also included those unobserved reflections for which $|F_c| > F_o/K$. The final agreement factors are R 0.055 (observed only) and 0.082 (including 378 unobserved reflections). The final value of $\left[\frac{\sum w(\Delta F)^2}{n-m} \right]^{1/2}$, with n 1245 and m 157, is 1.51.

Six strong reflections (with indices: 020, 040, 201, 131, 121 and 12 $\bar{1}$) which were probably affected by extinction were excluded from the refinement during its final stages.

The atomic scattering factors for carbon, oxygen, and nitrogen were taken from ref. 11, and for hydrogen from ref. 12.

RESULTS

The final atomic positional and thermal parameters along with their estimated standard deviations are listed in Tables 3 and 4 respectively. Observed and final calculated structure amplitudes are listed in Supplementary Publication No. SUP 20569 (14 pp., 1 microfiche).† Bond lengths and angles, and some intra- and inter-molecular non-bonded distances are given in Table 5 along with the

¹⁰ H. Hauptman and J. Karle, *Acta Cryst.*, 1954, **7**, 452.

¹¹ H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

¹² 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, p. 208.

TABLE 3

Atomic fractional co-ordinates, with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	0.5150(4)	0.4325(3)	0.1888(3)
O(2)	0.5695(3)	0.4111(2)	0.0980(2)
O(3)	0.6240(3)	0.3928(2)	0.2678(2)
C(4)	0.8038(4)	0.3209(3)	0.2421(3)
C(5)	0.2891(4)	0.5126(3)	0.3386(3)
O(6)	0.2302(4)	0.4401(2)	0.3972(2)
O(7)	0.3235(3)	0.6163(2)	0.3701(2)
C(8)	0.2711(6)	0.6380(4)	0.4805(3)
C(9)	0.2251(4)	0.5514(3)	0.1472(3)
C(10)	0.3358(4)	0.5015(3)	0.2242(2)
N(11)	0.0451(4)	0.6123(2)	0.1526(2)
C(12)	-0.0853(4)	0.6358(3)	0.2481(3)
C(13)	-0.0366(5)	0.6575(3)	0.0571(3)
H(14)	0.774(5)	0.274(3)	0.180(3)
H(15)	0.920(5)	0.368(3)	0.227(3)
H(16)	0.833(5)	0.276(3)	0.295(3)
H(17)	0.120(5)	0.618(3)	0.491(3)
H(18)	0.360(5)	0.592(3)	0.513(3)
H(19)	0.276(4)	0.721(3)	0.480(3)
H(20)	-0.095(5)	0.581(3)	0.290(3)
H(21)	-0.027(5)	0.697(3)	0.276(3)
H(22)	-0.235(5)	0.646(3)	0.227(3)
H(23)	0.064(5)	0.645(3)	-0.004(3)
H(24)	-0.191(5)	0.623(3)	0.044(3)
H(25)	-0.053(5)	0.740(3)	0.059(3)
H(26)	0.290(5)	0.541(3)	0.074(3)

TABLE 4

Anisotropic vibration parameters * ($U_{ij} \times 10^4 \text{ \AA}^2$), with estimated standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{31}
C(1)	457(17)	416(20)	550(23)	-16(15)	48(21)	31(17)
O(2)	739(14)	815(22)	555(17)	286(13)	-30(16)	96(12)
O(3)	502(11)	536(15)	562(15)	132(10)	-11(13)	-3(11)
C(4)	502(17)	582(23)	843(29)	146(16)	-73(22)	-35(17)
C(5)	418(16)	479(22)	566(24)	15(16)	27(24)	93(15)
O(6)	914(16)	570(16)	727(19)	-32(14)	148(16)	259(14)
O(7)	796(15)	565(16)	533(16)	-132(13)	-82(15)	103(12)
C(8)	1040(27)	904(33)	499(25)	16(22)	-159(27)	88(20)
C(9)	412(15)	416(19)	587(23)	-7(4)	-50(19)	24(15)
C(10)	409(14)	402(19)	451(21)	-5(14)	-4(20)	30(14)
N(11)	451(14)	508(17)	644(20)	73(13)	-51(18)	-19(13)
C(12)	479(17)	687(27)	860(30)	45(16)	-135(25)	97(18)
C(13)	662(20)	788(30)	761(28)	183(19)	51(25)	-125(19)

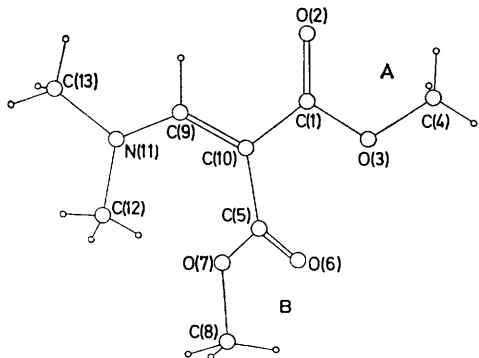
* In the form: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^{*b}U_{12} + 2klb^{*c}U_{23} + 2lhc^{*a}U_{31})]$.

FIGURE 1 A schematic drawing of the molecular framework showing the atom numbering system. The coplanar and twisted (see text) methoxycarbonyl groups are denoted by A and B

estimated standard deviations. The results of best-plane calculations are presented in Table 6 and Figures 1—3

TABLE 5

Bond angles and interatomic distances

(a) Bond distances (Å)			
C(1)—O(2)	1.223(5)	C(4)—H(14)	1.01(4)
C(1)—O(3)	1.344(5)	C(4)—H(15)	0.93(3)
O(3)—C(4)	1.438(4)	C(4)—H(16)	0.90(4)
C(5)—O(6)	1.200(5)	C(8)—H(17)	0.97(3)
C(5)—O(7)	1.344(5)	C(8)—H(18)	0.90(4)
O(7)—C(8)	1.461(5)	C(8)—H(19)	1.00(4)
C(1)—C(10)	1.443(4)	C(12)—H(20)	0.86(4)
C(5)—C(10)	1.487(5)	C(12)—H(21)	0.91(4)
C(9)—C(10)	1.380(5)	C(12)—H(22)	0.99(3)
C(9)—N(11)	1.337(4)	C(13)—H(23)	0.99(3)
N(11)—C(12)	1.456(5)	C(13)—H(24)	1.07(3)
N(11)—C(13)	1.464(5)	C(13)—H(25)	1.01(4)
		C(9)—H(26)	1.01(4)

(b) Bond angles (°)			
O(2)—C(1)—O(3)	121.6(3)	O(6)—C(5)—O(7)	123.1(4)
O(2)—C(1)—C(10)	125.9(3)	O(6)—C(5)—C(10)	126.0(4)
O(3)—C(1)—C(10)	112.5(3)	O(7)—C(5)—C(10)	111.0(3)
C(1)—O(3)—C(4)	117.6(3)	C(5)—O(7)—C(8)	115.6(3)
C(1)—C(10)—C(9)	115.8(3)	C(5)—C(10)—C(9)	126.6(3)
C(9)—N(11)—C(12)	124.7(3)	C(9)—N(11)—C(13)	119.7(3)
C(1)—C(10)—C(5)	117.6(3)	C(10)—C(9)—N(11)	131.0(3)
C(12)—N(11)—C(13)	115.6(3)		

(c) Intramolecular non-bonded distances (Å)			
C(5) ... C(12)	3.06	O(7) ... C(12)	3.08
O(3) ... O(6)	2.92	O(2) ... C(9)	2.77
O(2) ... C(4)	2.67	O(6) ... C(8)	2.65

(d) Intermolecular distances (Å)			
C(1) ... C(12 ^I)	3.61	C(1) ... C(4 ^{II})	3.40
O(3) ... C(4 ^{III})	3.30	C(4) ... C(4 ^{III})	3.55
O(7) ... C(12 ^{III})	3.43	O(2) ... C(9 ^{IV})	3.36
O(2) ... H(26 ^{IV})	2.39	O(3) ... C(8 ^V)	3.36
C(4) ... C(8 ^V)	3.60		

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at *x*, *y*, *z*:

$$\begin{array}{ll} \text{I } 1 + x, y, z & \text{IV } 1 - x, 1 - y, \bar{z} \\ \text{II } \frac{1}{2} + x, \frac{1}{2} - y, z & \text{V } 1 - x, 1 - y, 1 - z \\ \text{III } \frac{1}{2} + x, \frac{3}{2} - y, z & \end{array}$$

TABLE 6

Equations in terms of fractional co-ordinates of some best planes and, in square brackets, deviations (Å) of the atoms therefrom

Plane (1): C(1), O(2), O(3), C(4)	$3.764x + 9.629y - 0.157z = 6.082$
[C(1) -0.009, O(2) 0.005, O(3) 0.008, C(4) -0.004]	
Plane (2): C(5), O(6), O(7), C(8)	$5.947x - 2.633y + 3.147z = 1.451$
[C(5) 0.017, O(6) -0.009, O(7) -0.014, C(8) 0.007]	
Plane (3): C(9), C(10), N(11), C(12), C(13)	$3.359x + 10.106y + 1.973z = 6.632$
[C(9) -0.013, C(10) 0.007, N(11) 0.008, C(12) -0.004, C(13) 0.002]	
Plane (4): C(1), O(2), O(3), C(4), C(9), C(10), N(11), C(12), C(13)	$3.622x + 9.841y + 1.069z = 6.337$
[C(1) -0.014, O(2) -0.124, O(3) 0.076, C(4) -0.008, C(5) 0.117, O(6) -0.747, O(7) 1.296, C(8) 1.437, C(9) 0.062, C(10) 0.055, N(11) 0.015, C(12) -0.124, C(13) 0.062]	

display the molecular framework and two view of the packing arrangement respectively.

DISCUSSION

Packing and Thermal Motion.—The molecules of (I) are stacked along the *a* axis in such a way that the overlap of adjacent molecules is confined to contacts involving the C(12) and C(13) methyl groups and the oxygen

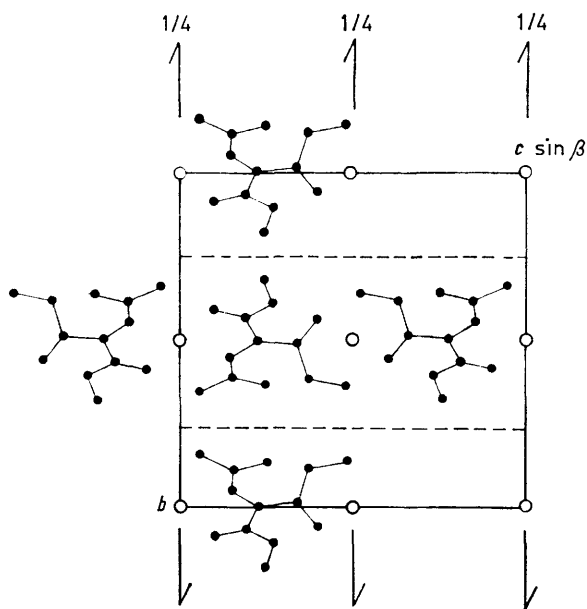


FIGURE 2 Projection of the structure down the stacking axis [100]

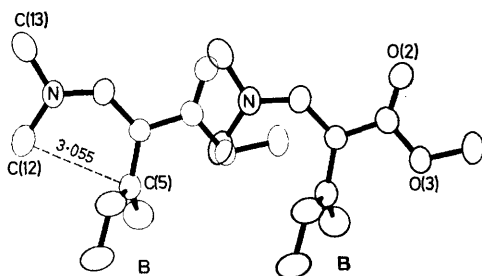


FIGURE 3 Projection of two stacked neighbours down the normal to the N(11) ... C(9) O(2) ... O(3) lines showing the twist of the B and overlap of the A methoxycarbonyl groups and dimethylamino-groups of the two molecules. Some distances (Å) in the region of overlap are O(2) ... C(13) 3.89, O(3) ... C(12) 3.46, and C(4) ... N(11) 3.99

atoms in the (A) methoxycarbonyl group in the neighbouring molecule (Figure 3). Neither these nor other C ... O contacts present in the structure, with the possible exception of C(9)–H(26) ... O(2), have a geometry which might suggest hydrogen bonding. The observed arrangement is thus probably due mainly to van der Waals interactions and, to some extent, to static dipolar interactions within, as well as, between the

stacks. There are no unacceptably short intermolecular contacts.

Although (I) cannot be, *a priori*, regarded as a rigid body, an analysis¹³ of the anisotropic vibration parameters has been performed in order to supplement the qualitative impression obtained from the comparison of packing with the individual vibration tensors. The root-mean-square discrepancy,* corrected for the number of the degrees of freedom, is 0.0071 Å² when all 13 heavy atoms are included in the calculation. Exclusion of O(6), O(7), and C(8) gives 0.0051 Å², indicating that the (B) methoxycarbonyl group vibrates, to some extent, independently of the rest of (I). This is consistent with the large separation of these groups along the stack and with their being involved in a small number of short contacts.

Molecular Structure.—The N(11)–C(9) bond distance of 1.337 Å, indicating a partial double-bond character of this linkage, and the fact that the nitrogen atom is coplanar with the three atoms bonded to it (Table 6), indicate that the state of hybridisation of the nitrogen is *sp*². It is not possible to say whether or not a minor deviation from planarity of the nitrogen could be concealed by the observed pattern of thermal motion, since either an inverting pyramid or a frozen-in disorder of differently oriented pyramids can, in principle, be hidden in our thermal ellipsoids. However, any such deviation must be very small. This can be appreciated by the structure¹⁴ of bisdimethylamino sulphone, in which the nitrogen is 0.27 Å from the plane of its bonded neighbours and the *p* character of the lone-pair calculated from the observed bond angles¹⁴ is found to be 93%. In our structure, however, the out-of-plane vibration amplitudes of N(11), C(12), and C(13) are 0.24, 0.26, and 0.30 Å and are probably mainly due to the molecular motion. Internal vibrations or disorder must be much smaller and consequently the *p* character of the lone-pair should in any case be close to 100%.

Except for the atoms O(6), O(7), and C(8), the molecule of (I) is roughly planar. The dimethylamino-group is almost exactly coplanar with the C(9)–C(10) bond in spite of the intramolecular overcrowding reflected in the C(5) ... C(12) distance of 3.055 Å (Figure 3). This would of course be relieved to some extent by rotating the NMe₂ group about the N(11)–C(9) bond, although such rotation would result in a partial loss of conjugation of the lone-pair of the nitrogen with the rest of the π system. The overcrowding is also reflected in the significantly increased bond angles on the concave side of the nearly planar C(5)–C(10)–C(9)–N(11)–C(12) system (Figure 1, Table 6). The present arrangement is more favourable, on steric grounds, than an arrangement in which both methoxycarbonyl groups are coplanar and the dimethylamino-group is twisted out of their plane. In that case, in addition to a close N(11) ... O(6) or

* The root-mean-square discrepancy is given by $[\sum(U_{ij}^{obs} - U_{ij}^{calc})^2 / (n - m)]^{1/2}$, where U_{ij}^{obs} atomic vibration parameters are given in Table 4, n is the number of independent U_{ij} values, and m is the number of rigid-body parameters.

¹³ V. Schomaker and K. N. Trueblood, *Acta Cryst.*, 1968, **B**, **24**, 63.

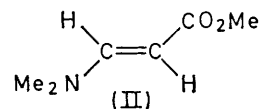
¹⁴ T. Jordan, H. W. Smith, J. Lohr, jun., and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 1963, **85**, 846.

N(11) ··· O(7) approach there would be an unfavourable proximity of the methoxycarbonyl oxygens. The C(9)–C(10) bond (1.380 Å) is significantly longer than a formal double-bond (1.337 Å)¹⁵ probably owing to the conjugation of this group with the lone-pair on the nitrogen atom and with the coplanar carbonyl in the (A) methoxycarbonyl group. The π bond-order of the C(9)–C(10) bond was calculated¹⁶ as 0.76 and supports the results of LCAO–MO calculations⁵ for a series of similarly polarised ethylene derivatives. Specifically, the C=C bond-order in 1-acetyl-1-benzoyl-2,2-bismethylthioethylene was calculated as 0.7543.⁵ The ΔG^* (79.9 °C) value for the isomerisation of this compound is 18.0 kcal mol⁻¹ *vs.* 15.6 kcal mol⁻¹ for (I) at 18.5 °C. The observed shortening of the C(10)–C(1) linkage (1.447 Å) as compared to expected C(sp²)–C(sp²) bond distances,¹⁷ and the normal length of the C(10)–C(5) bond (1.486 Å), which links C(10) with the twisted (B) methoxycarbonyl group, also appear to be consistent with this conjugation. The dimensions of both methoxycarbonyl groups agree well with those reported.¹⁷

The minimum energy of the molecule (I) is determined by a balance between steric factors and the magnitude of electron delocalisation. It would, therefore, be logical to extrapolate from the conformational structure in the solid state to that in solution. Supporting evidence for this assumption has been adduced from i.r. measurements (Table 7).^{18,19} Both in the solid state

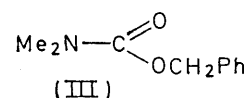
due to the large angle of twist (68°) from the main molecular plane as shown by the X-ray analysis. The π electrons of the twisted carbonyl C(5)=O(6) can be considered essentially localised, and therefore its stretching vibration occurs at a higher frequency relative to that of the conjugated methoxycarbonyl group (A). In any case, the present experimental results seem to justify conformational extrapolation of (I) from the solid, to isotropic solution.

If, as the experimental results (Table 7) indicate, the (B) methoxycarbonyl group is essentially excluded from participating in conjugation, then the magnitude of electron delocalisation in (I) should be comparable to that of the model compound, *trans*- β -dimethylaminoacrylate (II). Analysis of some physical data for the



two compounds illustrates this. Thus the C=C stretching frequencies of (I) and (II) (Table 7) are identical. Also, the ester carbonyl of (II), which is obviously coplanar with the π system, exhibits a stretching vibration at 1692 cm⁻¹, virtually identical with that which was previously assigned to the conjugated methoxycarbonyl group (A) (1694 cm⁻¹) of (I). Furthermore, the barrier to rotation about the Me₂N–C bond is considered to be a measure of the delocalisation energy of the system.²⁰ Comparison of the activation data of this process for compounds (I) and (II) (Table 7) again reveals close similarity.*

This evidence seems to justify the qualitative assumption that the magnitude of electron delocalisation in the



ground states of (I) and (II) must be similar. The difference in the rates of isomerisation about the C=C double bond in (I) and (II) should therefore be attributed mainly to the differential stability of the corresponding transition-states of the isomerisation process. Compound (II) is stable in the *trans*-configuration, and unfortunately no activation data is available for its isomerisation. In fact the *cis*-isomer has never been reported. We have attempted to isomerise (II) thermally by subjecting it to a temperature of 200 °C in 1-chloronaphthalene for 18 h, but aside from some decomposition products the *cis*-isomer was not detected (n.m.r. analysis). Photochemical irradiation of (II) in acetonitrile, acetone, cyclohexane, and benzene (sensitised with benzophenone)

TABLE 7

I.r. data and activation parameters for rotation about the Me₂N–C bond

Compound	I.r. stretching frequencies ^a cm ⁻¹		$\Delta G^*/$ kcal mol ⁻¹
	KBr	CCl ₄	
	C=O	C=C	
(I)	1729 1694	1614	13.3 (9.0 °C) ^c
(II)		1692	13.9 (0 °C) ^d
(III)		1614	15.9 (–1 °C) ^e

^a Recorded on a Perkin-Elmer grating i.r. spectrometer 257. ^b Resolution in solution was poorer than in the solid state. ^c Ref. 1; dichloromethane solution. ^d Ref. 18; chloroform solution. ^e Ref. 19; chloroform solution.

(KBr), and in solution (CCl₄), (I) exhibits two resolved carbonyl stretching bands at very similar frequencies. Furthermore, the C=C stretching band in the solid state occurs at a frequency identical with that which was determined in solution. The two carbonyl high and low stretching frequencies are assigned to the twisted ester (B) and the planar ester (A) respectively. The carbonyl of the (B) methoxycarbonyl group is incapable of effective conjugation with the rest of the π system. This must be

* The carbamate (III) isomerises significantly slower than its vinylogue (II), most probably owing to the extended conjugation in the latter system.

¹⁵ Ref. 12, p. 276.

¹⁷ *Chem. Soc. Special Publ.*, No. 12, 1956; No. 18, 1965.

¹⁶ C. A. Coulson, *Proc. Roy. Soc.*, 1939, A, **169**, 413.

¹⁸ H. E. A. Kramer and R. Gompper, *Z. phys. Chem.*, 1964, **43**, 292.

¹⁹ B. J. Price, R. V. Smallman, and I. Q. Sutherland, *Chem. Comm.*, 1966, 319.

²⁰ M. J. S. Dewar and P. Rona, *J. Amer. Chem. Soc.*, 1969, **91**, 2259.

employing a u.v. light source, for long periods of time were also futile. However, an upper limit of $3 \times 10^{-7} \text{ s}^{-1}$ (25 °C) has been established²¹ for the rate of the thermal isomerisation of the structurally similar *trans*-methyl β -cyclohexylaminoacrylate to its *cis*-isomer ($K_{\text{eq}} = (\textit{trans})/(\textit{cis}) = 0.22$). This rate value corresponds to $\Delta G^*(25 \text{ °C}) \geq 26.2 \text{ kcal mol}^{-1}$ and provides a good approximation for the isomerisation barrier of (II). For the isomerisation about the C=C double-bond of (I) we have previously determined $\Delta G^*(18.5 \text{ °C})$ as $15.6 \text{ kcal mol}^{-1}$. Thus, an additional methoxycarbonyl group substituted at the α -position of dimethylaminoacrylate lowers the barrier of isomerisation by at least $10.6 \text{ kcal mol}^{-1}$. However, the more important conclusion is that the rate enhancement should be attributed to the capacity of the malonate moiety of (I) to delocalise the negative charge in the dipolar transition state (Ia) rather than to ground-state electron delocalisation effects. If the difference in energy barriers of (I) and (II) is exclusively due to the differential stability of the two corresponding dipolar transition states, then it is expected to be equivalent to the differential stability of the anions of malonate and acetate. This has been calculated from the ionisation reactions²² of ethyl acetate and diethyl malonate to be $15.2 \text{ kcal mol}^{-1}$ ($\Delta\Delta G^\circ$ at 25°). If all our suppositions regarding the ground states of (I) and (II) are correct, then the present minimal energy difference of $10.6 \text{ kcal mol}^{-1}$ between the corresponding free energies of activation should approach $15.2 \text{ kcal mol}^{-1}$. It can then be implied that the free energy of activation for the isomerisation of (II) is *ca.* $15.6 + 15.2 = 30.8 \text{ kcal mol}^{-1}$.*

The activation energy for rotation about the $\text{R}_2\text{N-C}$

* While the kinetic data for (I) and (II) are for solutions in organic solvents of relatively low dielectric constants, the ionisation reactions of the malonate and acetate esters are for aqueous solutions, although, since in the ionisation reactions we are using an energy difference ($\Delta\Delta G^\circ$), the discrepancy should be minimised.

bond in (I) is a function of two inter-related molecular properties, namely the geometry of the nitrogen atom and the delocalisation energy of its lone-pair into the adjacent π system.²⁰ The nitrogen atom undergoes a change from its configuration in the ground state, which depends on the particular system, to sp^3 hybridisation in the transition state, where its lone-pair orbital is now orthogonal to the adjacent π system.²⁰ During this process delocalisation energy (ΔE_π) is lost and hybridisation energy (ΔE_h) is gained. The two terms are therefore related to the energy barrier for rotation about the $\text{R}_2\text{N-C}$ bond, $\Delta G^* = \Delta E_\pi - \Delta E_h$. The X-ray results indicate that the nitrogen atom in (I) is planar and therefore sp^2 hybridised, and the ΔG^* value for rotation about the $\text{R}_2\text{N-C}$ bond in (I) is $13.3 \text{ kcal mol}^{-1}$ (Table 7). This implies that the full value of the hybridisation energy of the nitrogen atom is gained upon rotation (90°) about the C(9)-N(11) bond. If ΔE_h ($sp^3 \rightarrow sp^2$) of the dimethylamino-nitrogen atom of (I) is taken to be equivalent to that of trimethylamine²³ ($6.9 \text{ kcal mol}^{-1}$), then the contribution of the nitrogen lone pair to the ground-state delocalisation energy can be approximated by: $\Delta E_\pi = 13.3 + 6.9 = 20.2 \text{ kcal mol}^{-1}$. Similarly for (II), $\Delta E_\pi = 20.8 \text{ kcal mol}^{-1}$. The small difference in the ΔE_π of (I) and (II) corroborates our previous argument based on the X-ray and i.r. data, that (I) possesses no significant extra delocalisation energy with respect to (II).

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²¹ K. Herbig, R. Huisgen, and H. Huber, *Chem. Rev.*, 1966, **99**, 2546.

²² R. G. Pearson and R. L. Dillon, *J. Amer. Chem. Soc.*, 1953, **75**, 2439.

²³ A. Rauk, J. D. Andose, W. G. Frick, R. Tang, and K. Mislow, *J. Amer. Chem. Soc.*, 1971, **93**, 6507.