# Variable-temperature NMR and X-Ray Crystallographic Studies of 5-Dimethylaminomethylene-, 5-Dimethylaminopropenylidene-, and 5-(5-Dimethylaminopenta-2,4-dienylidene)-Derivatives of Meldrum's Acid and Related Dimethyl Malonate Derivatives

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Variable-temperature ^{1}H and ^{13}C NMR studies of the title Meldrum's acid derivatives and the corresponding malonates show in most cases coalescence phenomena due to C–N and C=C rotation effects. The trends in free energies of activation for these processes are examined with respect to the X-ray crystal structures of the Meldrum's acid derivatives which show effects of electron delocalisation in the conjugated system.

There have been a number of studies of the electron delocalisation in the diacylenamine system 1, where restricted rotation about both the C–N and C=C bonds of the canonical form 1A
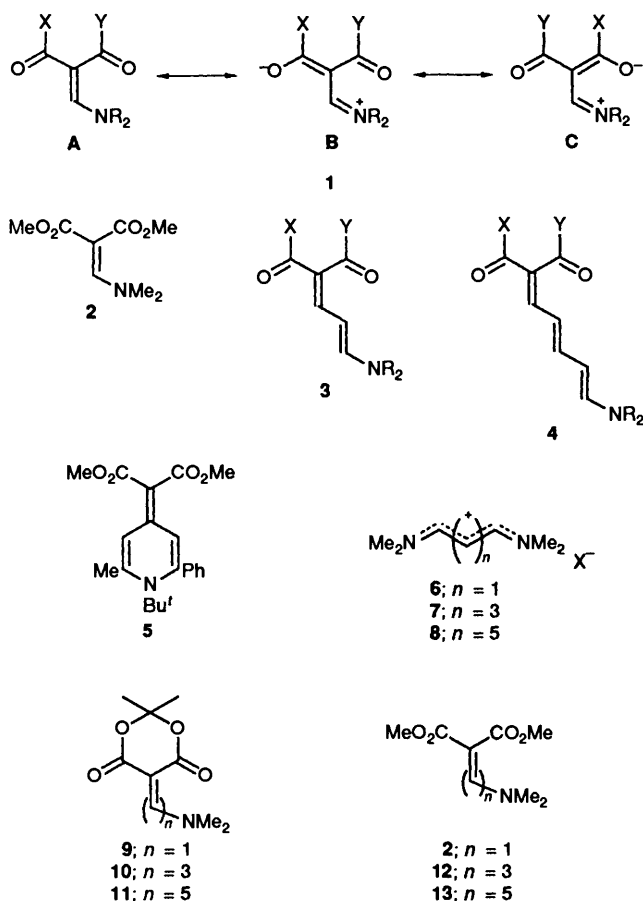
can be observed on the NMR time scale. The activation parameters for both of these processes have been shown to be dependent on the structural environment—the nature of the dicarbonyl group [1–3] (ketone, ester, amide, *etc.*), the incorporation of the dicarbonyl group into a ring,[1] the nature of the amino substituents R,[4] *etc.*—but the NMR conclusions have been supported by X-ray crystallographic work only in the case of the malonate 2.[2,3] Much less is known about the effect of extending the conjugation in these systems to diacyl-dienamines

3 and -trienamines 4, though Prokof'ev *et al.* have reported activation parameters for a number of dienes 3 (see below).[5] In addition restricted rotation about the C=C bond in heterofulvenes (*e.g.* 5) has been reported,[6] and both variable-temperature NMR [7,8] and X-ray crystallographic studies [9] of the polymethinium salts 6–8 have been carried out. In connection with other work,[10–13] we have prepared a series of Meldrum's acid (2,2-dimethyl-1,3-dioxane-4,6-dione) derivatives based on the structural units 1, 3 and 4, and have reported indirect evidence for C–N and C=C rotation phenomena in one case.[11] Here we present a more systematic approach to the problem, with variable-temperature NMR work on the Meldrum's acid derivatives 9–11 and the corresponding malonates 2, 12 and 13 supported by full structural data for the heterocyclic examples 9–11.

Results

Variable-temperature NMR.—The results of variable temperature NMR studies of the Meldrum's acid derivatives 9–11 and the dimethyl malonates 2, 12 and 13 are given in Table 1. Because of the marked solvent dependence of certain activation energies (*cf.* ref. 5) structurally similar solvents were chosen in most cases, with [^{2}H$_6$]acetone used for low temperature studies, and [^{2}H$_6$]dimethyl sulphoxide (DMSO) used for high temperature work. The data for C–N bond rotation were in all cases measured by the coalescence of the non-equivalent *N*-methyl group signals in the ^{1}H NMR spectra, and the temperatures quoted are accurate to ± 1 °C. For the Meldrum's acid derivatives, evidence for rotation about the C(5)=C(1') double bond was provided in the ^{13}C NMR spectra by coalescence of the C(4) and C(6) quaternary signals. This was difficult to measure accurately, not only because of the low intensity of these signals as coalescence approached, but also because of overlapping methine signals, particularly for the polymethine derivative 11. The error in these measurements is probably ± 5–10 °C, giving rise to an uncertainty in $\Delta G^{\ddagger}$ of ± 1–2 kJ mol^{-1}. Rotation around the corresponding C=C double bond of the malonates 2, 12 and 13 was shown by coalescence of the methoxy signals in the ^{1}H NMR spectrum and was not subject to substantial errors, in principle, though in two cases coalescence lay outside the temperature range of the spectrometer used. For the polymethine examples 10–13, we have no positive evidence for rotation about any other C=C or C–C bonds. These rotations would lead to alternative isomers which were not directly observable in the high temperature ^{13}C or ^{1}H

alternative isomers which were not directly observable in the high temperature ^{13}C or ^{1}H spectra, although in some cases the chemical shifts of the methine proton signals were temperature dependent.

The free energies of activation (Table 1) were obtained directly from the coalescence data. Our results are in reasonable agreement with available literature data (Table 1), except for the C=C rotation process of **12**. However the reported value[5] in

this case was obtained using methanol as the solvent, which is known to catalyse such C=C rotation, probably by hydrogen bonding to the ester groups; a reduction in T_c of up to 80 °C has been observed.[5] The measurement of entropy of activation was not attempted because it is subject to large errors, but the possibility of a substantial $\Delta S^{\ddagger}$ contribution (particularly for C=C rotation[4]) must be considered when comparing results obtained over a wide temperature range. Nevertheless, it is clear that in all cases, the activation energy for C–N rotation is greater in the Meldrum's series than for the corresponding open-chain compounds, whereas the reverse situation obtains for C=C rotation. This is consistent with the enhanced ability of a cyclic 1,3-dione system to stabilise a negative charge (**1B**, **C**)

Table 1 Variable-temperature NMR results

Compound	$T_c/°C^a$	$\Delta v/Hz^b$	$\Delta G^{\ddagger}/kJ\ mol^{-1\ c}$
C–N Rotation			
9	162[d]	54.2	90.5 (85.9)[1]
10	134[d]	40.1	85.5
11	50[f]	38.1	67.3
2	−7[f]	94.5	53.0 (55.6)[2]
12	19[f]	51.9	59.9 (61.3)[5]
13	−24[f]	47.2	50.9
C=C Rotation			
9	7[e]	265.9	53.5
10	130[d]	91.3	81.8
11	78[d,g]	108.2	70.3
2	25[f]	18.3	63.7 (65.2)[2]
12	⋙169[d,h]	8.4	⋙98 (91.1)[5]
13	>170[d,i]	10.6	>98

[a] Coalescence temperature. [b] Peak separation. [c] Values in parentheses are literature results. [d] [2H6]DMSO solution. [e] [2H]Chloroform. [f] [2H6]Acetone solution. [g] Particularly difficult to measure because of overlapping peaks: probable error in $T_c \pm 10$ °C. [h] No perceptible line broadening at this temperature. [i] Very significant broadening at 170 °C.

Table 2 Bond lengths/Å with standard deviations for **9**

O(1)–C(2)	1.443(4)	C(4)–C(5)	1.448(4)
O(1)–C(6)	1.344(3)	C(5)–C(6)	1.450(4)
C(2)–C(2A)	1.515(5)	C(5)–C(1′)	1.387(4)
C(2)–C(2B)	1.496(5)	C(6)–O(6)	1.222(4)
C(2)–O(3)	1.434(4)	C(1′)–N(1)	1.307(4)
O(3)–C(4)	1.352(4)	N(1)–C(1N)	1.444(4)
C(4)–O(4)	1.220(4)	N(1)–C(2N)	1.474(4)

Table 3 Angles/° with standard deviations for **9**

C(2)–O(1)–C(6)	118.26(21)	C(4)–C(5)–C(6)	117.72(24)
O(1)–C(2)–C(2A)	110.65(24)	C(4)–C(5)–C(1′)	125.8(3)
O(1)–C(2)–C(2B)	105.39(24)	C(6)–C(5)–C(1′)	115.15(25)
O(1)–C(2)–O(3)	108.73(22)	O(1)–C(6)–C(5)	117.44(24)
C(2A)–C(2)–C(2B)	113.7(3)	O(1)–C(6)–O(6)	116.9(3)
C(2A)–C(2)–O(3)	110.38(24)	C(5)–C(6)–O(6)	125.6(3)
C(2B)–C(2)–O(3)	107.78(25)	C(5)–C(1′)–N(1)	131.4(3)
C(2)–O(3)–C(4)	118.25(23)	C(1′)–N(1)–C(1N)	121.2(3)
O(3)–C(4)–O(4)	117.1(3)	C(1′)–N(1)–C(2N)	123.0(3)
O(3)–C(4)–C(5)	116.53(25)	C(1N)–N(1)–C(2N)	115.7(3)
O(4)–C(4)–C(5)	126.0(3)		

Table 5 Atomic coordinates with esds for **9**

	x	y	z
O(1)	0.838 75(18)	0.216 00(22)	0.643 40(17)
C(2)	0.889 8(3)	0.330 6(3)	0.740 5(3)
C(2A)	0.885 8(4)	0.272 4(4)	0.865 4(3)
C(2B)	1.023 4(3)	0.364 4(4)	0.741 6(4)
O(3)	0.814 90(20)	0.469 22(22)	0.703 97(20)
C(4)	0.684 8(3)	0.458 3(3)	0.668 23(25)
O(4)	0.624 71(22)	0.578 09(23)	0.662 90(21)
C(5)	0.629 2(3)	0.307 3(3)	0.628 31(24)
C(6)	0.710 3(3)	0.192 1(3)	0.599 23(24)
O(6)	0.671 89(20)	0.075 00(24)	0.537 29(20)
C(1′)	0.498 9(3)	0.270 3(3)	0.590 82(25)
N(1)	0.405 75(24)	0.324 7(3)	0.625 70(21)
C(1N)	0.273 5(3)	0.275 4(4)	0.565 2(3)
C(2N)	0.428 5(3)	0.431 6(4)	0.732 6(3)

Table 6 Bond lengths/Å with standard deviations for **10**

O(1)–C(2)	1.438(7)	C(5)–C(6)	1.417(8)
O(1)–C(6)	1.371(7)	C(5)–C(1′)	1.409(8)
C(2)–C(2A)	1.509(9)	C(6)–O(6)	1.225(7)
C(2)–C(2B)	1.513(9)	C(1′)–C(2′)	1.385(8)
C(2)–O(3)	1.411(7)	C(2′)–C(3′)	1.397(8)
O(3)–C(4)	1.389(7)	C(3′)–N(1)	1.305(7)
C(4)–O(4)	1.193(7)	N(1)–C(1N)	1.474(8)
C(4)–C(5)	1.449(8)	N(1)–C(2N)	1.458(8)

Table 7 Angles/° with standard deviations for **10**

C(2)–O(1)–C(6)	117.1(4)	C(4)–C(5)–C(1′)	120.9(5)
O(1)–C(2)–C(2A)	109.6(5)	C(6)–C(5)–C(1′)	117.4(5)
O(1)–C(2)–C(2B)	105.8(5)	O(1)–C(6)–C(5)	116.9(5)
O(1)–C(2)–O(3)	110.1(4)	O(1)–C(6)–O(6)	116.1(5)
C(2A)–C(2)–C(2B)	112.4(5)	C(5)–C(6)–O(6)	126.9(5)
C(2A)–C(2)–O(3)	111.7(5)	C(5)–C(1′)–C(2′)	130.6(5)
C(2B)–C(2)–O(3)	107.1(5)	C(1′)–C(2′)–C(3′)	116.6(5)
C(2)–O(3)–C(4)	118.3(4)	C(2′)–C(3′)–N(1)	126.7(5)
O(3)–C(4)–O(4)	117.9(5)	C(3′)–N(1)–C(1N)	119.7(5)
O(3)–C(4)–C(5)	114.2(5)	C(3′)–N(1)–C(2N)	124.4(5)
O(4)–C(4)–C(5)	127.9(5)	C(1N)–N(1)–C(2N)	116.0(5)
C(4)–C(5)–C(6)	121.7(5)		

Table 4 Torsion angles/° with standard deviations for **9**

C(6)–O(1)–C(2)–C(2A)	73.3(3)	O(3)–C(4)–C(5)–C(1′)	178.5(3)
C(6)–O(1)–C(2)–C(2B)	−163.37(25)	O(4)–C(4)–C(5)–C(6)	158.4(3)
C(6)–O(1)–C(2)–O(3)	−48.0(3)	O(4)–C(4)–C(5)–C(1′)	−7.9(5)
C(2)–O(1)–C(6)–C(5)	15.0(4)	C(4)–C(5)–C(6)–O(1)	18.1(4)
C(2)–O(1)–C(6)–O(6)	−165.35(25)	C(4)–C(5)–C(6)–O(6)	−161.5(3)
O(1)–C(2)–O(3)–C(4)	51.2(3)	C(1′)–C(5)–C(6)–O(1)	−174.23(24)
C(2A)–C(2)–O(3)–C(4)	−70.4(3)	C(1′)–C(5)–C(6)–O(6)	6.2(4)
C(2B)–C(2)–O(3)–C(4)	164.9(3)	C(4)–C(5)–C(1′)–N(1)	−32.0(5)
C(2)–O(3)–C(4)–O(4)	165.1(3)	C(6)–C(5)–C(1′)–N(1)	161.5(3)
C(2)–O(3)–C(4)–C(5)	−20.6(4)	C(5)–C(1′)–N(1)–C(1N)	175.1(3)
O(3)–C(4)–C(5)–C(6)	−15.3(4)	C(5)–C(1′)–N(1)–C(2N)	−8.7(5)

Table 8 Torsion angles/° with standard deviations for 10

C(6)–O(1)–C(2)–C(2A)	73.3(6)		O(4)–C(4)–C(5)–C(6)	172.1(6)
C(6)–O(1)–C(2)–C(2B)	−165.3(5)		O(4)–C(4)–C(5)–C(1′)	−4.0(9)
C(6)–O(1)–C(2)–O(3)	−49.9(6)		C(4)–C(5)–C(6)–O(1)	6.3(8)
C(2)–O(1)–C(6)–C(5)	22.1(7)		C(4)–C(5)–C(6)–O(6)	−169.2(6)
C(2)–O(1)–C(6)–O(6)	−161.9(5)		C(1′)–C(5)–C(6)–O(1)	−177.4(5)
O(1)–C(2)–O(3)–C(4)	51.8(6)		C(1′)–C(5)–C(6)–O(6)	7.1(9)
C(2A)–C(2)–O(3)–C(4)	−70.2(6)		C(4)–C(5)–C(1′)–C(2′)	−0.1(9)
C(2B)–C(2)–O(3)–C(4)	166.3(5)		C(6)–C(5)–C(1′)–C(2′)	−176.4(6)
C(2)–O(3)–C(4)–O(4)	157.3(5)		C(5)–C(1′)–C(2′)–C(3′)	−179.0(6)
C(2)–O(3)–C(4)–C(5)	−25.1(7)		C(1′)–C(2′)–C(3′)–N(1)	179.3(5)
O(3)–C(4)–C(5)–C(6)	−5.2(8)		C(2′)–C(3′)–N(1)–C(1N)	179.7(6)
O(3)–C(4)–C(5)–C(1′)	178.7(5)		C(2′)–C(3′)–N(1)–C(2N)	0.9(9)

Table 9 Atomic coordinates with esds for 10

	x	y	z
O(1)	0.3824(4)	0.4070(5)	0.6252(3)
C(2)	0.4401(5)	0.2385(7)	0.6355(4)
C(2A)	0.3487(6)	0.0926(8)	0.6028(5)
C(2B)	0.5047(6)	0.2483(9)	0.5628(5)
O(3)	0.5267(3)	0.2157(5)	0.7421(3)
C(4)	0.4936(4)	0.2408(7)	0.8267(5)
O(4)	0.5518(4)	0.1713(6)	0.9110(3)
C(5)	0.3927(4)	0.3572(7)	0.8012(4)
C(6)	0.3406(5)	0.4478(7)	0.7011(4)
O(6)	0.2667(4)	0.5664(6)	0.6770(3)
C(1′)	0.3470(4)	0.3928(7)	0.8781(4)
C(2′)	0.3826(4)	0.3327(7)	0.9831(4)
C(3′)	0.3168(5)	0.3913(7)	1.0387(4)
N(1)	0.3342(4)	0.3498(5)	1.1372(4)
C(1N)	0.2562(6)	0.4245(9)	1.1840(5)
C(2N)	0.4288(5)	0.2342(8)	1.2079(5)

Table 10 Bond lengths/Å with standard deviations for 11

O(1)–C(2)	1.433(4)	C(5)–C(1′)	1.403(5)
O(1)–C(6)	1.372(5)	C(6)–O(6)	1.216(5)
C(2)–C(2A)	1.509(6)	C(1′)–C(2′)	1.368(5)
C(2)–C(2B)	1.501(6)	C(2′)–C(3′)	1.401(5)
C(2)–O(3)	1.432(4)	C(3′)–C(4′)	1.376(5)
O(3)–C(4)	1.375(4)	C(4′)–C(5′)	1.400(5)
C(4)–O(4)	1.218(4)	C(5′)–N(1)	1.305(5)
C(4)–C(5)	1.435(5)	N(1)–C(1N)	1.459(6)
C(5)–C(6)	1.435(5)	N(1)–C(2N)	1.456(5)

Table 11 Angles/° with standard deviations for 11

|			
C(2)–O(1)–C(6)	118.2(3)	C(6)–C(5)–C(1′)	117.2(3)
O(1)–C(2)–C(2A)	110.0(3)	O(1)–C(6)–C(5)	117.0(3)
O(1)–C(2)–C(2B)	105.7(3)	O(1)–C(6)–O(6)	115.9(3)
O(1)–C(2)–O(3)	109.6(3)	C(5)–C(6)–O(6)	127.1(4)
C(2A)–C(2)–C(2B)	113.5(3)	C(5)–C(1′)–C(2′)	131.9(4)
C(2A)–C(2)–O(3)	110.2(3)	C(1′)–C(2′)–C(3′)	120.2(4)
C(2B)–C(2)–O(3)	107.7(3)	C(2′)–C(3′)–C(4′)	126.4(4)
C(2)–O(3)–C(4)	118.3(3)	C(3′)–C(4′)–C(5′)	118.9(3)
O(3)–C(4)–O(4)	116.5(3)	C(4′)–C(5′)–N(1)	126.3(4)
O(3)–C(4)–C(5)	116.4(3)	C(5′)–N(1)–C(1N)	121.3(4)
O(4)–C(4)–C(5)	126.9(3)	C(5′)–N(1)–C(2N)	122.6(3)
C(4)–C(5)–C(6)	120.2(3)	C(1N)–N(1)–C(2N)	116.0(3)
C(4)–C(5)–C(1′)	122.5(3)		

and is the same factor which causes Meldrum's acid to be a much stronger acid than acyclic dialkyl malonates.[14] Alternatively, efficient overlap between the ring oxygen atoms and the carbonyl groups is not possible in the cyclic series, thus increasing the importance of conjugation with the exocyclic nitrogen atoms.

There is no consistent trend in $\Delta G^{\ddagger}$ values throughout the individual series of Meldrum's acid (9–11) and malonate (2, 12 and 13) derivatives, though for well-established steric reasons[1] the results for the first member of each series (9 and 2) would be expected to be anomalous (see below). Otherwise, an increase in the length of the polymethine chain causes a smooth decrease in $\Delta G^{\ddagger}$ for both C–N and C=C rotation: this is probably a consequence of the delocalisation of the lone pair of the nitrogen atom over an increased number of atoms, thereby reducing the average bond order in the conjugated system. Similar results have been observed in a series of polymethinium salts.[7,8]

X-Ray Crystallography.—The bond lengths, bond angles, torsion angles and fractional coordinates of the Meldrum's acid derivatives 9–11 are given in Tables 2–13, and pertinent data on these and on selected model compounds are displayed in Fig. 1. ORTEP plots for 9–11 giving the crystallographic numbering schemes are shown in Figs. 2–4.

The geometry of the monomethine derivative 9 may be compared with the corresponding monomethylamino compound 14[15] (and the related O- and S-methyl analogues 15 and 16[15]) and with the open-chain dimethylaminomethyl-enemalonate 2.[3] Despite the structural variations (which

9A   9B
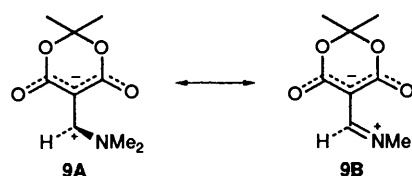
include an intramolecular hydrogen bond in 14, and the reversed configuration of one of the ester groups in 2), the majority of the bond lengths in all three compounds are closely similar. However, the C(1′)–N, and the *cisoid* C(5)–carbonyl bond lengths are significantly shorter in 14, where these form part of a hydrogen bonded chelate ring, and the corresponding parameters are significantly longer in the open-chain compound 2. The relative magnitude of the C–N bond lengths, in particular [1.307(4) Å in 9, and 1.337(4) Å in 2] show the increase in double bond character in the Meldrum's acid derivative, which is reflected in the high value of $\Delta G^{\ddagger}$ for C–N rotation (see above). Indeed, the lengths of the C–N bonds are comparable to those of the vinamidinium salt [6; 1.308(9) Å][16] for which, by reasons of symmetry, delocalisation must be essentially complete. This analogy extends to the C=C bond lengths of 9, 2 and 6 [1.387(4); 1.380(5); and 1.381(8) Å respectively] all of which are identical with those of benzenoid derivatives [1.380(13) Å].[17]

The bond angles around the C(5) position in 9 are greatly distorted in comparison with those in other Meldrum's acid derivatives,[15] and there is significant deviation from planarity around this atom. In addition, there is a large dihedral angle

Table 12 Torsion angles/° with standard deviations for 11

C(6)–O(1)–C(2)–C(2A)	− 72.9(4)		O(4)–C(4)–C(5)–C(1′)	4.3(6)
C(6)–O(1)–C(2)–C(2B)	164.2(3)		C(4)–C(5)–C(6)–O(1)	− 6.6(5)
C(6)–O(1)–C(2)–O(3)	48.4(4)		C(4)–C(5)–C(6)–O(6)	170.6(4)
C(2)–O(1)–C(6)–C(5)	− 21.8(5)		C(1′)–C(5)–C(6)–O(1)	178.2(3)
C(2)–O(1)–C(6)–O(6)	160.7(3)		C(1′)–C(5)–C(6)–O(6)	− 4.6(6)
O(1)–C(2)–O(3)–C(4)	− 49.5(4)		C(4)–C(5)–C(1′)–C(2′)	1.8(6)
C(2A)–C(2)–O(3)–C(4)	71.7(4)		C(6)–C(5)–C(1′)–C(2′)	176.9(4)
C(2B)–C(2)–O(3)–C(4)	− 164.0(3)		C(5)–C(1′)–C(2′)–C(3′)	− 178.1(4)
C(2)–O(3)–C(4)–O(4)	−159.6(3)		C(1′)–C(2′)–C(3′)–C(4′)	179.0(4)
C(2)–O(3)–C(4)–C(5)	23.7(4)		C(2′)–C(3′)–C(4′)–C(5′)	− 179.3(4)
O(3)–C(4)–C(5)–C(6)	5.7(5)		C(3′)–C(4′)–C(5′)–N(1)	− 178.2(4)
O(3)–C(4)–C(5)–C(1′)	− 179.4(3)		C(4′)–C(5′)–N(1)–C(1N)	179.3(4)
O(4)–C(4)–C(5)–C(6)	− 170.6(4)		C(4′)–C(5′)–N(1)–C(2N)	1.3(6)

Table 13 Atomic coordinates with esds for 11

	x	y	z
O(1)	0.560 85(20)	0.184 1(3)	0.964 34(16)
C(2)	0.625 5(3)	0.225 1(4)	1.063 29(24)
C(2A)	0.692 8(4)	0.083 3(5)	1.118 3(3)
C(2B)	0.532 0(4)	0.287 4(5)	1.099 6(3)
O(3)	0.708 58(21)	0.350 4(3)	1.068 83(16)
C(4)	0.783 9(3)	0.335 3(4)	1.018 06(24)
O(4)	0.874 48(22)	0.417 2(3)	1.044 35(17)
C(5)	0.743 9(3)	0.231 2(4)	0.936 48(23)
C(6)	0.625 9(3)	0.160 5(5)	0.906 3(3)
O(6)	0.575 04(23)	0.086 0(4)	0.832 80(19)
C(1′)	0.812 2(3)	0.203 6(4)	0.878 9(3)
C(2′)	0.923 2(3)	0.257 5(5)	0.884 7(3)
C(3′)	0.970 0(3)	0.214 4(5)	0.814 6(3)
C(4′)	1.078 9(3)	0.261 5(5)	0.810 8(3)
C(5′)	1.111 2(3)	0.208 4(4)	0.734 7(3)
N(1)	1.212 04(25)	0.239 1(4)	0.722 12(21)
C(1N)	1.236 1(5)	0.175 3(7)	0.640 1(4)
C(2N)	1.308 4(3)	0.333 8(5)	0.789 7(3)

about the C(5)–C(1′) double bond (ca. 30°) in this molecule (Table 4 and Fig. 5) caused by the steric congestion in the region of O(4) which is not present in either 10 or 11 (corresponding dihedral angle < 5°). This factor raises the ground-state energy of 9 and is presumably responsible for the especially facile C=C rotation in this compound (Table 1).* It is of interest that the dihedral angles around the C(1′)–N bond are much smaller (5–9°) which indicates that resonance stabilisation (9A ⟷ 9B) is possible.

14; X = NH
15; X = O
16; X = S

17
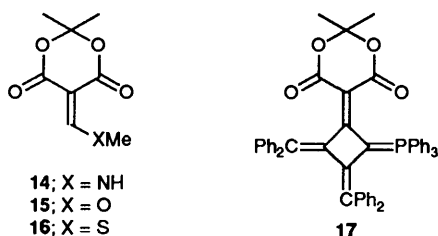
A most remarkable feature of the structures of 10 and 11 is that, in the polymethine chain, the lengths of the formal C–C single bonds are consistently shorter than those of the formal C=C double bonds (Fig. 1). Although these differences are not individually statistically significant, the extensive delocalisation which contributes to C–N and C=C rotation is clearly evident. Although the bond lengths of the extended enaminone 18[19] (Fig. 1) are of comparable magnitude their relative order is reversed, evidence of the much weaker conjugation in this system.

* Similar conclusions have been drawn recently from a study of the cyclobutenylidene Meldrum's acid derivative 17.[18]

The C–N bond lengths are almost identical across the series 9–11 (Fig. 1), which confirms [20] that simple ideas of ground state delocalisation cannot completely account for the trends in $\Delta G^{\ddagger}$ values. Indeed the C=C bond length in 9 is notably shorter than in 10 or 11 even though rotation in 9 is the most facile.

Whereas the bond lengths of the Meldrum's ring of 9 and 11 are highly symmetrical about the C(2)–C(5) plane, those of 10 show some evidence of preferred delocalisation to the carbonyl group which is trans to the conjugated chain. This C=O bond is long [1.225(7) Å] and is associated with an unusually short C(6)–C(5) ring bond [1.417(8) Å]. The data for the corresponding cis group are C(4)–C(5) 1.449(8) Å and C=O 1.193(7) Å, so the effect, if present, is at the limit of accuracy of the data (ca. 2 esds).

The bond angles around C(5) in 10 and 11 show that, unlike in 9, planarity in this region of the molecule is maintained, but that the bond angle at C(1′) remains large (> 130°) despite the much less severe steric constraints. Along the conjugated chains, the bond angles alternate between large (> 125°) and small (generally < 120°) which appears to be a common effect in such polymethine chains.[21] Overall, the conjugated systems in 10 and 11 deviate little from planarity (Figs. 6 and 7).

Discussion

The major conclusions from the variable-temperature NMR results may be summarised as follows. First, comparing the Meldrum's series 9, 10 and 11 with the corresponding malonates 2, 12 and 13, the activation energies for C–N rotation are uniformly greater in the former group, with that for the monomethine example 9 being particularly large. Conversely, the energies for C=C rotation are smaller for the heterocyclic examples; these activation energies for both monomethine cases 2 and 9 are particularly small. For the tri- and penta-methine cases (10 and 11; 12 and 13) the energies of both C–N and C=C rotation decrease with increasing chain length.

In placing these results in a structural context, it is clear that —as pointed out by Jackman[20]—estimates of ground-state delocalisation do not give a good guide to rotation barriers. Thus the energies for C–N and C=C rotation are not complementary, as might be suggested from structures 1A–C. The anomalous results for the first members of the series 9 and 2 are predominantly due to the effects of crowding rather than to substantial bond-length differences. This crowding is relieved in the case of 2 by the reversal of configuration of one ester group, which allows the dimethylaminomethylene group to remain essentially planar,[3] and in the case of 9 by twisting about the C(5)–C(1′) bond (structures 9A and 9B). The net effect is that in 9 the C=C activation energy is slightly lowered and the conjugation 9A ⟷ 9B results in a shorter C–N bond length and a substantial increase in the energy for C–N rotation.

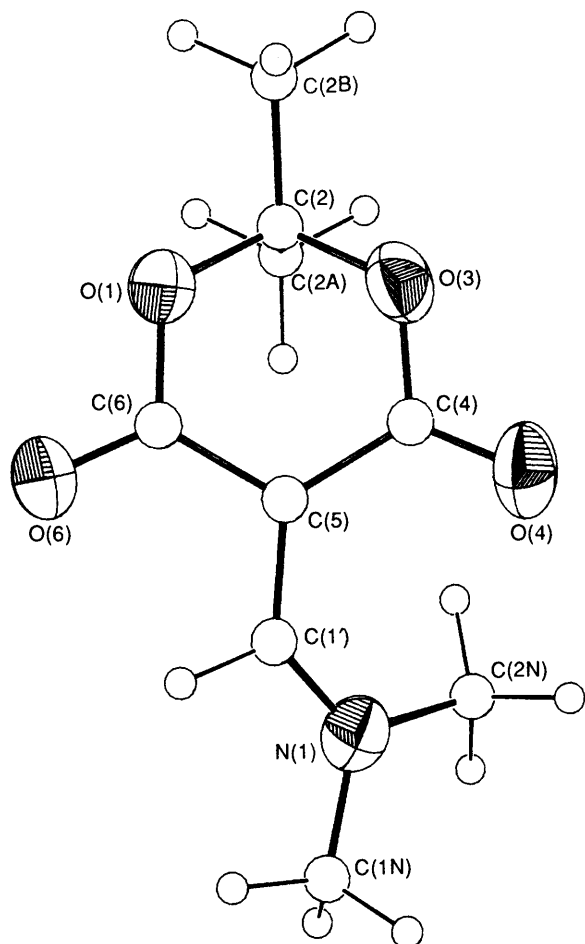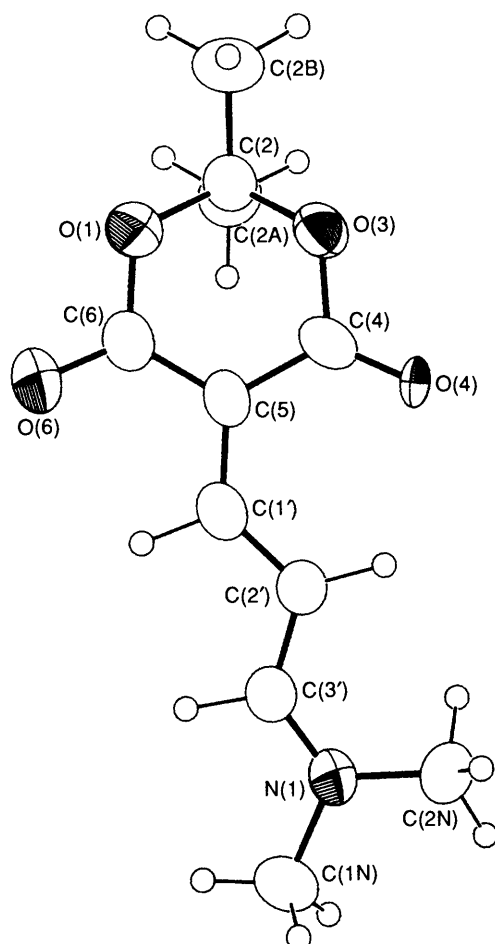It is clear from the X-ray structures that such complicating

Fig. 1 Selected structural parameters for 9–11 and related model compounds

steric effects are essentially absent in the higher homologues 10 and 11 (and, by implication 12 and 13). These have essentially planar conjugated systems with clear evidence of delocalisation in the short C–N and C–C bond lengths and long C=C bond lengths. However, the differences in free energies of activation (Table 1) between 10 and 11, and the expected differences in average bond order, are not reflected in any significant changes in bond lengths. Similar results have also been found in a series of azamethinium salts.[22]

Experimental

Ambient and variable-temperature ^{1}H and ^{13}C NMR results were obtained at 200 and 50 MHz, respectively, on a Bruker WP200SY spectrometer unless stated otherwise. Coupling constants are in Hz. Routine spectra were obtained for [^{2}H]chloroform solutions. The variable-temperature results are shown in Table 1.

Meldrum's Acid Derivatives 9–11.—The dimethylamino-methylene-[10] and dimethylaminopropenylidene-[12] derivatives 9 and 10 were made as previously described. Reaction of Meldrum's acid (1.08 g, 7.5 mmol) with *N,N*-dimethyl-aminopentadienal[23] (1.00 g, 8 mmol) in pyridine (8 cm[3]) for 18 h[24] gave 5-(5-*dimethylaminopenta*-2,4-*dienylidene*)-2,2-*di-*

methyl-1,3-*dioxane*-4,6-*dione* as a purple solid after removal of the solvent and trituration with ethanol; (1.35 g, 72%), m.p. 215 °C (from ethanol) (Found: C, 62.5; H, 6.85; N, 5.85. $C_{13}H_{17}NO_4$ requires C, 62.15; H, 6.75; N, 5.6%); δ_H 7.81 (1 H, d, ^3J 12.7), 7.1–7.4 (3 H, m), 5.58 (1 H, t, ^3J 11.8), 3.18 (3 H, br), 2.96 (3 H, br) and 1.62 (6 H, s); δ_C(20 MHz) 165.16 (q), 162.77 (q), 162.51, 158.08, 157.25, 103.18, 102.81, 95.74 (q), 92.93 (q), 45.2, 37.6 (methyl carbon atom signals are broad at room temperature due to restricted rotation) and 26.84; m/z 251 (M[+], 68%), 164 (12), 121 (28), 120 (24) and 105 (100).

Dimethyl N,N-*Dimethylaminomethylenemalonate and its Vinylogues.*[25]—The appropriate 5-substituted 2,2-dimethyl-1,3-dioxane-4,6-dione (2 mmol) was dissolved in methanol (10 cm[3]) and was treated with a solution of sodium methoxide [from sodium (0.1 g, 4 mmol) in methanol (8 cm[3])] and the mixture was stirred at room temperature for 2–16 h. The solvent was removed *in vacuo* and the residual anion was dissolved in dimethylformamide. Anhydrous potassium carbonate (0.55 g, 4 mmol) and methyl iodide (1.42 g, 10 mmol) were added and the mixture was stirred at room temperature overnight. The mixture was filtered, water (20 cm[3]) was added and the system was extracted with diethyl ether (3 × 20 cm[3]). The combined

Fig. 2 ORTEP plot of **9** showing crystallographic numbering scheme

Fig. 3 ORTEP plot of **10** showing crystallographic numbering scheme

Table 14 Crystal data

	9	**10**	**11**
Molecular formula	$C_9H_{13}NO_4$	$C_{11}H_{15}NO_4$	$C_{13}H_{17}NO_4$
M	199.21	225.25	251.29
Crystal system	Monoclinic	Monoclinic	Monoclinic
$a/\text{Å}$	11.012(4)	12.415(3)	11.879(4)
$b/\text{Å}$	8.656(3)	7.5521(18)	8.482(3)
$c/\text{Å}$	11.316(4)	13.615(4)	14.917(7)
$\beta/°$	110.140(27)	114.649(18)	111.65(3)
$V/\text{Å}^3$	1013	1160	1397
Space group	$P2_1/c$	$P2_1/a$	$P2_1/c$
Z	4	4	4
$D_x/\text{g cm}^{-3}$	1.306	1.290	1.195
Crystal	Colourless plate	Yellow needle	Red plate
Crystal dimensions/mm	0.655 × 0.46 × 0.21	0.385 × 0.27 × 0.077	0.84 × 0.28 × 0.016
$\mu(\text{Cu-K}\alpha)/\text{cm}^{-1}$	7.79	7.34	6.54

Table 15 Data collection and processing

	9	**10**	**11**
Diffractometer		Stoë STADI-4 four-circle	
Scan mode	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$
Radiation/Å		Graphite-monochromated Cu-Kα, λ = 1.541 84	
θ range/°	5–60	5–60	5–60
Index range h	$-12 \longrightarrow 12$	$-13 \longrightarrow 13$	$-13 \longrightarrow 13$
k	$0 \longrightarrow 9$	$0 \longrightarrow 8$	$0 \longrightarrow 9$
l	$0 \longrightarrow 12$	$0 \longrightarrow 15$	$0 \longrightarrow 16$
Data measured	1611	1841	2199
Data used	$1256[I \geqslant 3\sigma(I)]$	$920[I \geqslant 3\sigma(I)]$	$1246[I \geqslant 2\sigma(I)]$

Table 16 Structure analysis and refinement

	9	10	11
Method of solution		Automatic direct methods [27]	
Method of refinement		Full-matrix least-squares [28]	
Treatment of H atoms		Fixed geometry, except for rigid methyl group on N	
Anisotropic refinement		All non-H atoms	
Weighting scheme (w^{-1})	$\sigma^2(F) + 0.000\ 12F^2$	$\sigma^2(F) + 0.001\ 17F^2$	$\sigma^2(F) + 0.000\ 10F^2$
Final R, R_W	0.0707, 0.0964	0.0613, 0.0823	0.0524, 0.0649
Final ΔF synthesis max., min. residues/e Å^{-3}	0.42, -0.38	0.29, -0.26	0.19, -0.22
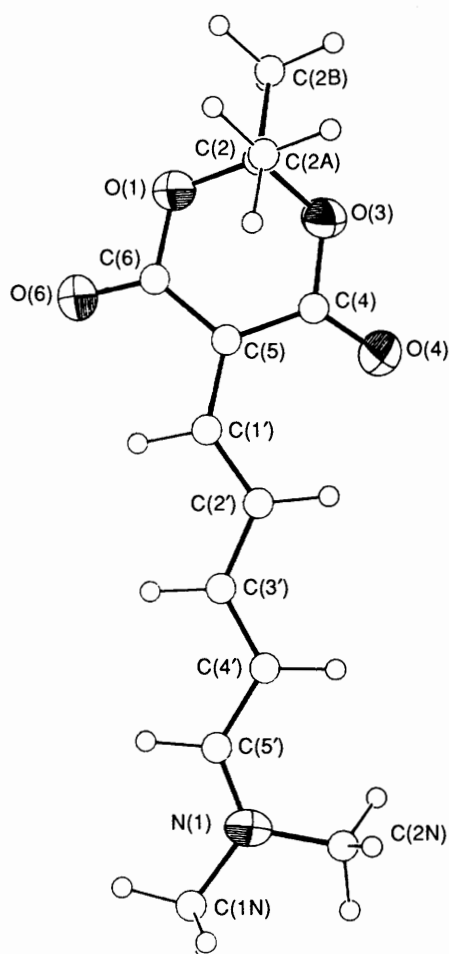
Fig. 4 ORTEP plot of **11** showing crystallographic numbering scheme
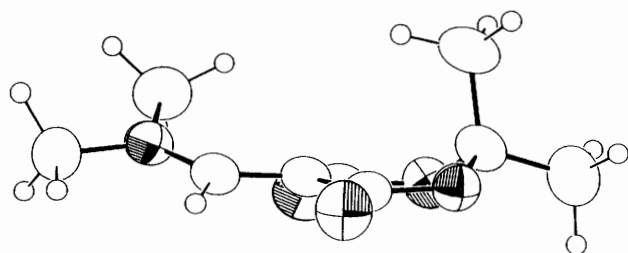
Fig. 5 Side view of **9**

organic layers were dried ($MgSO_4$) and the solvent was removed *in vacuo*. The following dimethyl malonates were obtained.

N,N-dimethylaminomethylene- [from 5-(*N,N*-dimethylaminomethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione treated with sodium methoxide for 5 h] (40 mg, 11%), b.p. 150 °C (0.1 Torr *) [lit.,[2] 115 °C (0.05 Torr)].

* 1 Torr = 133 Pa.
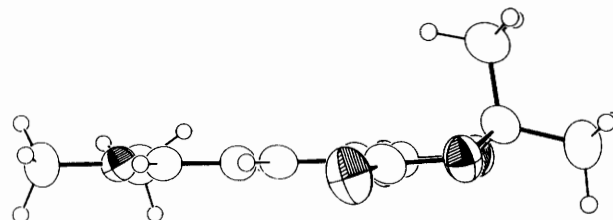
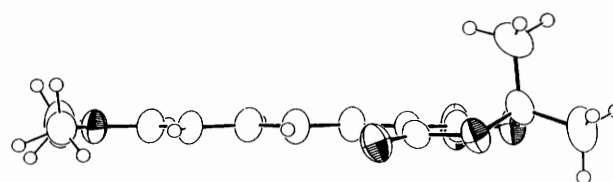**Fig. 6** Side view of **10**

Fig. 7 Side view of **11**

N,N-Dimethylaminopropenylidene [5] [from 5-(*N,N*-dimethyl-aminopropenylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione treated with sodium methoxide for 2 h] (134 mg, 32%), b.p. 185 °C (0.1 Torr), as an oil, which solidified (lit.,[26] m.p. 105–106 °C) (Found: C, 56.4; H, 7.2; N, 6.45. $C_{10}H_{15}NO_4$ requires C, 56.3; H, 7.05; N, 6.55%); δ_H 7.65 (1 H, d, ^3J 12.5), 6.88 (1 H, d, ^3J 12.2), 6.04 (1 H, t, ^3J 12.4), 3.67 (3 H, s), 3.61 (3 H, s) and 2.91 (6 H, br s); δ_C 167.10 (q), 166.95 (q), 156.84, 154.03, 105.27 (q), 97.06, 50.88, 50.63 and 29.25 (br); m/z 213 (M$^+$, 100%), 182 (87), 113 (26), 94 (50) and 82 (56).

N,N-*Dimethylaminopenta-2,4-dienylidene* [from 5-(s-*N,N*-di-methylaminopenta-2,4-dienylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione treated with sodium methoxide for 16 h] (240 mg, 50%), b.p. 220 °C (0.05 Torr), as an oil which solidified (Found: C, 60.3; H, 7.3; N, 5.65. $C_{12}H_{17}NO_4$ requires C, 60.25; H, 7.1; N, 5.85%); δ_H 7.56 (1 H, d, ^3J 12.1), 6.47–6.86 (3 H, m), 5.22 (1 H, dd, ^3J 11.4 and 12.4), 3.79 (3 H, s), 3.73 (3 H, s) and 2.90 (6 H, s); δ_C 166.71 (q), 166.52 (q), 151.14 (2C), 150.88, 115.87, 112.26 (q), 99.28, 51.35, 51.19 and 40.48; m/z 239 (M$^+$, 22%), 177 (100), 150 (45), 136 (36), 108 (31), 105 (39) and 77 (50).

X-Ray Crystallography.—Details of crystal data, data collection and processing, and structure analysis and refinement for **9–11** are given in Tables 14–16. Selected molecular geometry parameters [29] and refined fractional coordinates are recorded in Tables 2–13. Illustrations were prepared using ORTEP.[30] Tables of thermal parameters and calculated hydrogen-atom positions have been deposited at the Cambridge Crystallographic Data Centre (CCDC).†

† For details of the CCDC deposition scheme, see 'Instructions for Authors (1991)', *J. Chem. Soc., Perkin Trans. 2*, 1991, issue 1.

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