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Two *N*-Aminoazolylmethylene Derivatives of Meldrum's Acid

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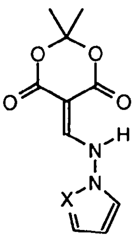
Abstract

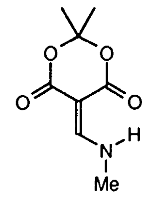
The structures of two derivatives of Meldrum's acid, 2,2-dimethyl-5-[*N*-(1-pyrrolyl)aminomethylene]-1,3-dioxane-4,6-dione, $C_{11}H_{12}N_2O_4$, (1), and 2,2-dimethyl-5-[*N*-(1-pyrazolyl)aminomethylene]-1,3-dioxane-4,6-dione, $C_{10}H_{11}N_3O_4$, (2), which differ only at one position in the five-membered ring, are described.

Comment

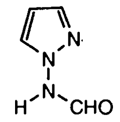
The title compounds (1) and (2) were synthesized as part of a pyrolysis study aimed at the preparation of novel heterocyclic compounds (Blake, McNab, Morrow & Rataj, 1993). The crystal structures were determined because of the current interest in the structures of *N*-aminoazoles (de la Concepcion Foces-Foces, Cano, Claramunt, Sanz, Catalan, Fabero, Fruchier & Elguero, 1990; Salazar, Espada, Sanz, Claramunt, Elguero, Garcia-Granda, Diaz & Gomez-Beltran, 1993) and because of our interest in hydrogen bonding in aminomethylene Meldrum's acid derivatives (Blake, Hunter & McNab, 1989).



(1) X = CH
(2) X = N



(3)



(4)

The *N*-aminopyrrolyl derivative (1) crystallized with two molecules in the asymmetric unit. One of these, designated by unprimed atoms, showed the effects of slight disorder, which gave less reliable molecular parameters for the region around C7. Fortunately, no such problem occurred in the other molecule, which is defined by primed atoms.

The aminomethylene Meldrum's acid moiety shows no significant differences between structures (1) and (2). The presence of hydrogen bonding between O4 and H8 [O4···N8 2.746 (5) and 2.710 (3) Å in (1) and (2), respectively] induces detectable asymmetry in the Meldrum's acid unit; C4—O4 is significantly longer than C6—O6 and C4—C5 is significantly shorter than C5—C6 in both cases. This asymmetry is also reflected in the bond angles around C5. [Note that the atomic coordinates and bond lengths for (2) should be compared with the equivalent primed atomic coordinates and bond lengths in (1) because of the disorder affecting the molecule defined by unprimed atoms in (1).] In methylaminomethylene Meldrum's acid (3) the quality of the diffraction data were generally inadequate to identify such deviations (Blake *et al.*, 1989). The bond lengths within the *N*-aminopyrazolyl unit are very similar to those reported for *N*-(pyrazol-1-yl)formamide (4) (Salazar *et al.*, 1993).

There are some significant differences between the valence angles involving the *N*-aminoazole units in (1) and (2), particularly at the ring heteroatom N9. The angles within the pyrazole ring in (2) are, however, very similar to those in the formamide (4) (Salazar *et al.*, 1993).

The atoms O4, C4, C5, C6, O6, C7 and N8 show small r.m.s. deviations from their best planes of 0.04 (5) and 0.013 (3) Å for (1) and (2), respectively. The corresponding deviations from the planes defined by N8, N9, C10, C11, C12 and C13 in (1) and N8, N9, N10, C11, C12 and C13 in (2) are 0.004 (6) and 0.003 (4) Å, respectively. The interplanar angles of 70.3 (2) and 41.26 (5)° in (1) and (2), respectively, are much smaller than the value of 85.5° seen in *N*-(pyrazol-1-yl)formamide (4) (Salazar *et al.*, 1993). These lower values may reflect the fact that the Meldrum's acid group promotes more extensive delocalization of the N8 lone pair than does the formyl group.

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In (1) and (2) there is both intra- and intermolecular hydrogen bonding, the latter linking molecules related by a crystallographic inversion centre to form centrosymmetric dimers, as shown in Figs. 1 and 2.

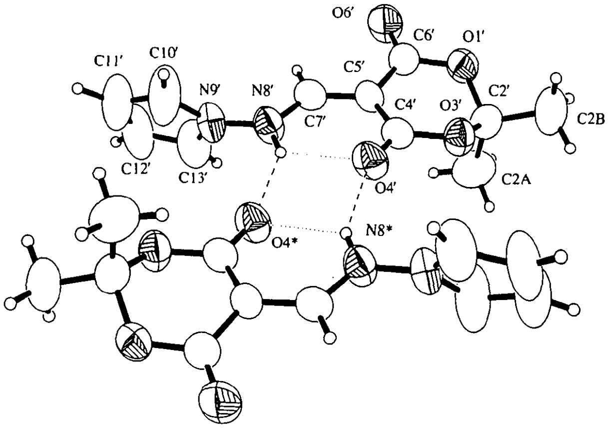

Fig. 1. A view of one hydrogen-bonded dimer of (1). The molecules are related by inversion through $(0, -\frac{1}{2}, \frac{1}{2})$. The intramolecular O4'···N8' and O4'···H8' distances are 2.746 (5) and 2.12 (5) Å, respectively, and the O4'···N8* and O4'···H8* intermolecular contacts are 2.917 (5) and 2.12 (5) Å, respectively. Displacement ellipsoids are shown at the 50% probability level.

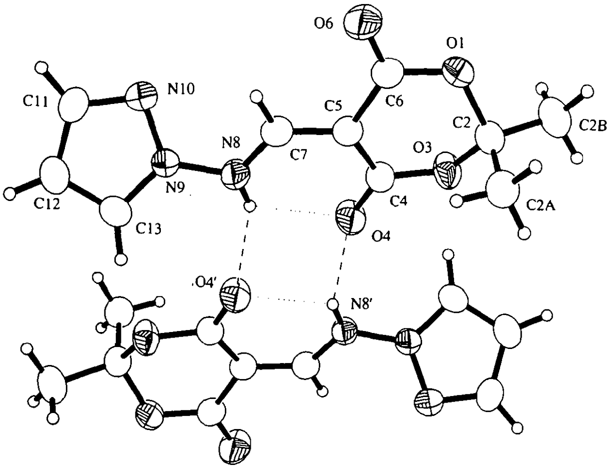

Fig. 2. A view of the hydrogen-bonded dimer of (2). The molecules are related by inversion through $(\frac{1}{2}, 0, -\frac{1}{2})$. The intramolecular O4···N8 and O4···H8 distances are 2.710 (3) and 2.14 (2) Å, respectively, and the O4···N8' and O4···H8' intermolecular contacts are 2.902 (3) and 2.12 (2) Å, respectively. Displacement ellipsoids are shown at the 50% probability level.

Experimental

Compound (1)

Crystal data

$C_{11}H_{12}N_2O_4$
$M_r = 236.23$
Monoclinic
$P2_1/c$
$a = 16.7900\ (11)$ Å
$b = 12.6423\ (8)$ Å
$c = 11.1014\ (6)$ Å
$\beta = 94.31\ (6)°$
$V = 2349.8\ (2)$ Å^3
$Z = 8$
$D_x = 1.335$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 30 reflections
$\theta = 17–18°$
$\mu = 0.871$ mm^{-1}
$T = 293\ (2)$ K
Needle
0.62 × 0.10 × 0.08 mm
Yellow

Data collection

Stoe Stadi-4 diffractometer
ω–2θ scans
Absorption correction: none
3088 measured reflections
3088 independent reflections
1915 observed reflections $[I > 2\sigma(I)]$

$\theta_{\max} = 59.33°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 12$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity variation: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0563$
$wR(F^2) = 0.1475$
$S = 1.192$
3087 reflections
315 parameters
H atoms placed in calculated positions except for H8 and H8'
$w = 1/[\sigma^2(F_o^2) + (0.0717P)^2 + 1.7512P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.086$

$\Delta\rho_{\max} = 0.672$ e Å^{-3}
$\Delta\rho_{\min} = -0.274$ e Å^{-3}
Extinction correction: *SHELXL93* (Sheldrick, 1993)
Extinction coefficient: 0.0013 (2)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (1)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	0.18522 (15)	0.0447 (2)	0.5331 (3)	0.0675 (8)
C2	0.2254 (2)	−0.0012 (3)	0.6387 (4)	0.0580 (11)
C2*A*	0.2485 (3)	0.0832 (3)	0.7302 (4)	0.0681 (12)
C2*B*	0.1695 (3)	−0.0830 (4)	0.6821 (4)	0.0806 (14)
O3	0.2956 (2)	−0.0570 (2)	0.6080 (2)	0.0599 (8)
C4	0.3459 (2)	−0.0059 (3)	0.5373 (4)	0.0579 (11)
O4	0.4138 (2)	−0.0372 (2)	0.5355 (3)	0.0789 (9)
C5	0.3115 (2)	0.0796 (3)	0.4662 (4)	0.0580 (11)
C6	0.2273 (3)	0.0994 (4)	0.4559 (4)	0.0641 (11)
O6	0.1911 (2)	0.1569 (3)	0.3840 (3)	0.0992 (12)
C7	0.3560 (3)	0.1510 (4)	0.3970 (4)	0.085 (2)
N8	0.4296 (3)	0.1475 (3)	0.3916 (4)	0.0862 (12)
N9	0.4623 (3)	0.2377 (4)	0.3338 (4)	0.0885 (13)
C10	0.4982 (4)	0.2322 (6)	0.2286 (5)	0.113 (2)
C11	0.5191 (4)	0.3296 (7)	0.2016 (6)	0.114 (2)
C12	0.4950 (4)	0.3964 (5)	0.2889 (8)	0.119 (2)
C13	0.4575 (3)	0.3396 (5)	0.3705 (6)	0.092 (2)
O1'	0.31446 (14)	−0.0024 (2)	0.0485 (3)	0.0620 (8)
C2'	0.2772 (2)	−0.1038 (3)	0.0605 (4)	0.0613 (11)
C2*A*'	0.2680 (3)	−0.1273 (4)	0.1912 (4)	0.089 (2)
C2*B*'	0.3273 (3)	−0.1815 (4)	−0.0026 (5)	0.091 (2)
O3'	0.20018 (14)	−0.1043 (2)	−0.0063 (2)	0.0590 (8)
C4'	0.1509 (2)	−0.0223 (3)	0.0107 (3)	0.0488 (10)
O4'	0.07989 (15)	−0.0331 (2)	−0.0206 (2)	0.0618 (8)
C5'	0.1857 (2)	0.0724 (3)	0.0601 (3)	0.0474 (9)
C6'	0.2716 (2)	0.0853 (3)	0.0721 (4)	0.0569 (10)
O6'	0.3073 (2)	0.1662 (2)	0.0954 (3)	0.0792 (10)

C7′	0.1400 (2)	0.1556 (3)	0.0914 (3)	0.0523 (10)
N8′	0.0614 (2)	0.1613 (3)	0.0842 (3)	0.0580 (9)
N9′	0.0244 (2)	0.2479 (3)	0.1302 (3)	0.0589 (9)
C10′	−0.0173 (3)	0.3201 (5)	0.0653 (5)	0.109 (2)
C11′	−0.0435 (3)	0.3928 (5)	0.1412 (5)	0.101 (2)
C12′	−0.0158 (3)	0.3645 (5)	0.2541 (5)	0.104 (2)
C13′	0.0264 (3)	0.2747 (5)	0.2477 (4)	0.092 (2)

Table 2. *Selected geometric parameters* (Å, °) *for* (1)

O1—C6	1.343 (5)	O1′—C6′	1.359 (5)
O1—C2	1.430 (5)	O1′—C2′	1.436 (5)
C2—O3	1.436 (4)	C2′—O3′	1.442 (4)
C2—C2*B*	1.500 (5)	C2′—C2*B*′	1.500 (6)
C2—C2*A*	1.504 (6)	C2′—C2*A*′	1.501 (6)
O3—C4	1.360 (5)	O3′—C4′	1.349 (4)
C4—O4	1.208 (5)	C4′—O4′	1.224 (4)
C4—C5	1.434 (6)	C4′—C5′	1.424 (5)
C5—C6	1.432 (6)	C5′—C7′	1.363 (5)
C5—C7	1.432 (6)	C5′—C6′	1.446 (5)
C6—O6	1.209 (5)	C6′—O6′	1.204 (4)
C7—N8	1.242 (5)	C7′—N8′	1.318 (5)
N8—N9	1.438 (5)	N8′—N9′	1.375 (4)
N8—H8	1.10 (5)	N8′—H8′	0.90 (4)
N9—C13	1.355 (6)	N9′—C10′	1.330 (6)
N9—C10	1.355 (6)	N9′—C13′	1.345 (5)
C10—C11	1.321 (8)	C10′—C11′	1.343 (7)
C11—C12	1.370 (9)	C11′—C12′	1.352 (7)
C12—C13	1.348 (8)	C12′—C13′	1.344 (7)
O4—C4—O3	118.9 (4)	O4′—C4′—O3′	118.0 (3)
O4—C4—C5	125.4 (4)	O4′—C4′—C5′	124.4 (4)
O3—C4—C5	115.7 (3)	O3′—C4′—C5′	117.5 (3)
C6—C5—C7	113.4 (4)	C7′—C5′—C4′	121.6 (3)
C6—C5—C4	122.1 (4)	C7′—C5′—C6′	117.7 (4)
C7—C5—C4	124.5 (4)	C4′—C5′—C6′	120.6 (3)
O6—C6—O1	117.9 (4)	O6′—C6′—O1′	118.2 (3)
O6—C6—C5	127.1 (4)	O6′—C6′—C5′	126.4 (4)
O1—C6—C5	115.0 (4)	O1′—C6′—C5′	115.4 (3)
N8—C7—C5	124.3 (5)	N8′—C7′—C5′	127.4 (4)
C7—N8—N9	114.0 (5)	C7′—N8′—N9′	120.0 (3)
C7—N8—H8	120 (3)	C7′—N8′—H8′	118 (3)
N9—N8—H8	124 (3)	N9′—N8′—H8′	121 (3)
C13—N9—C10	110.4 (5)	C10′—N9′—C13′	109.1 (4)
C13—N9—N8	125.9 (5)	C10′—N9′—N8′	125.4 (4)
C10—N9—N8	123.6 (5)	C13′—N9′—N8′	125.5 (4)
C11—C10—N9	106.9 (6)	N9′—C10′—C11′	108.3 (5)
C10—C11—C12	108.4 (6)	C10′—C11′—C12′	107.1 (5)
C13—C12—C11	109.0 (6)	C13′—C12′—C11′	108.7 (5)
C12—C13—N9	105.2 (6)	C12′—C13′—N9′	106.8 (4)
C6—C5—C7—N8	−179.1 (4)	C6′—C5′—C7′—N8′	178.0 (4)
C4—C5—C7—N8	−0.7 (7)	C4′—C5′—C7′—N8′	1.5 (6)
C5—C7—N8—N9	−169.8 (4)	C5′—C7′—N8′—N9′	173.9 (4)
C7—N8—N9—C10	−115.4 (6)	C7′—N8′—N9′—C10′	112.1 (5)
C7—N8—N9—C13	60.1 (7)	C7′—N8′—N9′—C13′	−66.0 (6)

Compound (2)

Crystal data

$C_{10}H_{11}N_3O_4$
$M_r = 237.22$
Triclinic
$P\bar{1}$
$a = 5.4407$ (10) Å
$b = 10.341$ (2) Å
$c = 10.714$ (2) Å
$\alpha = 107.351$ (7)°
$\beta = 96.814$ (11)°
$\gamma = 100.900$ (15)°
$V = 555.1$ (2) Å^3
$Z = 2$
$D_x = 1.419$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 10$–11°
$\mu = 0.112$ mm^{-1}
$T = 295$ (2) K
Tablet
0.85 × 0.42 × 0.22 mm
Pale yellow

Data collection

Stoe Stadi-4 diffractometer
ω–2θ scans
Absorption correction: none
3031 measured reflections
1964 independent reflections
1640 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0079$
$\theta_{\rm max} = 25.02°$
$h = -6 \rightarrow 6$
$k = -12 \rightarrow 11$
$l = 0 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity variation: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0318$
$wR(F^2) = 0.0691$
$S = 0.181$
1964 reflections
159 parameters
H atoms placed in fixed, calculated positions except for H8N
$w = 1/[\sigma^2(F_o^2) + (0.1000P)^2 + 10P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.225$

$\Delta\rho_{\rm max} = 0.198$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.139$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0303 (25)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	0.3845 (2)	0.33589 (12)	0.53163 (11)	0.0451 (3)
C2	0.2829 (3)	0.3651 (2)	0.6519 (2)	0.0400 (4)
C2*A*	0.1407 (3)	0.4778 (2)	0.6619 (2)	0.0503 (4)
C2*B*	0.5046 (3)	0.4020 (2)	0.7641 (2)	0.0561 (5)
O3	0.1148 (2)	0.24049 (12)	0.65565 (11)	0.0446 (3)
C4	−0.0623 (3)	0.1646 (2)	0.54585 (15)	0.0364 (4)
O4	−0.2431 (2)	0.08212 (12)	0.55771 (11)	0.0486 (3)
C5	−0.0186 (3)	0.1819 (2)	0.42169 (15)	0.0350 (3)
C6	0.2205 (3)	0.2664 (2)	0.4139 (2)	0.0398 (4)
O6	0.2894 (3)	0.27468 (14)	0.31268 (12)	0.0605 (4)
C7	−0.1803 (3)	0.1019 (2)	0.3042 (2)	0.0361 (3)
N8	−0.3938 (2)	0.01040 (14)	0.29094 (13)	0.0376 (3)
N9	−0.5191 (2)	−0.07735 (14)	0.16566 (12)	0.0369 (3)
N10	−0.3816 (3)	−0.1272 (2)	0.07411 (14)	0.0464 (4)
C11	−0.5589 (3)	−0.2050 (2)	−0.0310 (2)	0.0511 (5)
C12	−0.8036 (3)	−0.2061 (2)	−0.0057 (2)	0.0512 (5)
C13	−0.7716 (3)	−0.1219 (2)	0.1224 (2)	0.0457 (4)

Table 4. *Selected geometric parameters* (Å, °) *for* (2)

O1—C6	1.362 (2)	C6—O6	1.209 (2)
O1—C2	1.434 (2)	C7—N8	1.315 (2)
C2—O3	1.446 (2)	N8—H8N	0.87 (2)
C2—C2*A*	1.502 (2)	N8—N9	1.383 (2)
C2—C2*B*	1.501 (2)	N9—N10	1.344 (2)
O3—C4	1.350 (2)	N9—C13	1.341 (2)
C4—O4	1.220 (2)	N10—C11	1.324 (2)
C4—C5	1.435 (2)	C11—C12	1.388 (3)
C5—C7	1.373 (2)	C12—C13	1.358 (2)
C5—C6	1.450 (2)		
O4—C4—O3	118.03 (14)	N10—N9—N8	119.14 (12)
O4—C4—C5	124.35 (14)	C13—N9—N8	127.01 (13)
O3—C4—C5	117.55 (13)	C11—N10—N9	102.89 (13)
C7—C5—C4	121.20 (14)	N10—C11—C12	112.3 (2)
C7—C5—C6	117.54 (14)	C13—C12—C11	105.2 (2)
C4—C5—C6	120.39 (14)	N9—C13—C12	105.74 (15)
C4—C5—C7—N8	4.6 (3)	C7—N8—N9—N10	36.9 (2)
C6—C5—C7—N8	173.9 (2)	C7—N8—N9—C13	−143.8 (2)
C5—C7—N8—N9	−170.62 (14)		

In both structures the H atoms on N were located from a ΔF synthesis; the positions of these H atoms were allowed to refine with $U_{iso} = 1.2 \times U_{eq}$ of the corresponding N atom. Data collection and cell refinement: *DIF*4 (Stoe & Cie, 1988*a*). Data reduction: *REDU*4 (Stoe & Cie, 1988*b*). Structure solution: *SHELXS*86 (Sheldrick, 1990). Structure refinement: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1992).

We thank the SERC for provision of a four-circle diffractometer and Lonza Ltd for a gift of Meldrum's acid.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1120). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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α-Pyrone at 150 K

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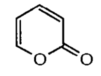
Abstract

We have determined the crystal structure of the low-melting α-pyrone (2-pyrone, $C_5H_4O_2$) at 150 K. The C—C bond distances within the ring exhibit substantial bond-length alternation, indicating that the molecule may be described largely in terms of a localized bond model. The α-pyrone molecules are packed in a herringbone fashion in the unit cell.

Comment

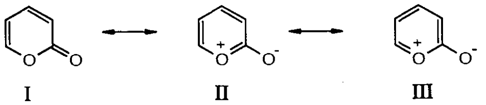
We are involved in determining the structures of fundamental parent compounds which are the simplest representatives of their class. Apart from their inherent interest, these obviously fulfil a valuable role as reference structures, for example in molecular modelling and theoretical studies. The effort required to obtain single crystals from liquid samples such as α-pyrone, (1), is therefore justified.



(1)

α-Pyrones are valuable synthetic reagents in organic chemistry; for example, they can behave as dienes in Diels–Alder reactions (Boulton & McKillop, 1984). However, inferences regarding their electronic structure have been drawn largely from chemical and spectroscopic data, as the crystal structures of α-pyrones determined so far have been of analogues incorporating π-active functional groups which perturb the pyrone ring.

The crystal structure of α-pyrone consists of discrete $C_4H_5O_2$ molecules (Fig. 1). Although the C—C bond distances within the ring are shorter than formal C_{sp^2}—C_{sp^2} single bonds (typically 1.48 Å), there is substantial bond-length alternation, consistent with C3—C4 and C5—C6 being strongly π-bonded [1.339 (4) and 1.338 (4) Å, respectively] and C2—C3 and C4—C5 being more weakly so [1.439 (4) and 1.424 (4) Å, respectively]. This imples that of the three formal valence canonical forms which define the electronic structure of α-pyrone shown in the scheme below, form I is dominant, with only minor contributions from forms II and III. The electronic structure of α-pyrone is, therefore, essentially localized.



These features are reminiscent of the structure of furan (C—C 1.34 and 1.42 Å; C—O 1.36 Å), for which they have also been interpreted as being symptomatic of rather limited delocalization. These results not withstanding, there are considerable differences between the bond lengths of the lactone function in α-pyrone and standard values for δ-lactones derived from the analysis of structures in the Cambridge Structural Database (Schweizer & Dunitz, 1982; Norskov-Lauritsen, Bürgi,

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