Conformational Studies of 2,3-Diacyl-5-nitrocyclopentadienes: Delocalized Systems With Very Short Intramolecular O · · · H · · · O Hydrogen Bonds. Crystal and Molecular Structures of 2,3-Diacetyl- and 2,3-Dibenzoyl-5-nitrocyclopentadiene

By **George Ferguson,*** **Wayne C. Marsh,** and **Roderic J. Restivo,** Department of Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1
Douglas Lloyd, Chemistry Department, The University, St. Andrews, Fife, Scotland

Crystals of (IVa) 2,3-diacetyl-5-nitrocyclopentadiene and of the dibenzoyl analogue (IVb) are monoclinic, space group $P2_1/c$, with $Z = 4$; unit-cell dimensions: (IVa) $a = 5.115(1)$, $b = 10.780(2)$, $c = 16.126(2)$ Å, $\beta = 90.38(2)°$; (IVb) $a = 14.241(2)$, $b = 7.441(1)$, $c = 19.433(2)$ Å, $\beta = 131.49(1)°$. Both structures were solved from diffractometer data by direct methods and refined by least-squares calculations to R 0.044 [1 226 observed reflections, (IVa)] and 0.039 [1 690 observed reflections, (IVb)]. In both molecules, in the solid state, the enolic hydrogen is midway between the two oxygen atoms and forms a short symmetrical intramolecular O · · · H · · · O hydrogen bond [O · · · O 2.433(2) (IVb) and 2.446(2) Å (IVa)]. This results in a symmetrically delocalized structure. There is a small amount of conjugation between the nitro-groups and cyclopentadiene rings. The molecular packing may give rise to weak charge-transfer effects. In (IVb) the molecules are stacked in infinite columns parallel to b, interplanar separations 3.18 and 3.33 Å; in (IVa) there are discrete pairs of molecules, interplanar spacing 3.32 Å.

2,3-DIACYL-5-NITROCYCLOPENTADIENES were first prepared by condensation of nitromalondialdehyde with appropriate diketones.[1] More recently, they have been obtained by nitration of 2-acyl-6-hydroxyfulvenes.[2]

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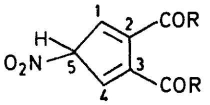
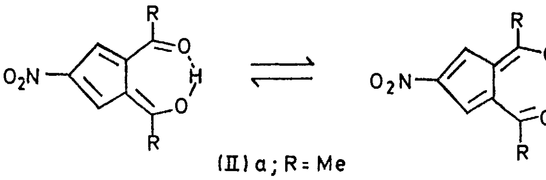
[1] W. J. Hale, *J. Amer. Chem. Soc.*, 1912, **34**, 1580; *Ber.*, 1912, **45**, 1596.

[2] D. Lloyd and N. W. Preston, *J. Chem. Soc.* (*C*), 1969, 2464.

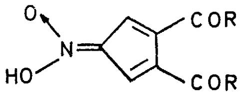
They were originally assigned structure (I), but the n.m.r. spectrum of (Ia) showed that it almost certainly had the fulvenoid structure (IIa),[2,3] although the alternative but less likely structure (IIIa) was not entirely ruled out. In place of the rapid tautomeric equilibrium (II) a symmetric delocalized structure (IV) may be suggested.[2]



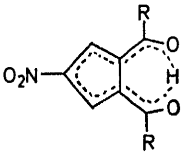
(I) a; R = Me
b; R = Ph



(II) a; R = Me



(III) a; R = Me



(IV) a; R = Me
b; R = Ph

X-Ray structural analyses of 2,3-diacetyl- and 2,3-dibenzoyl-5-nitrocyclopentadiene were undertaken and established structures (IVa) and (IVb) respectively.

EXPERIMENTAL

For each compound preliminary unit-cell and space-group data were determined from Weissenberg and precession photographs. Accurate cell-parameters and orientation matrix were obtained by a least-squares procedure applied to 12 carefully measured reflections on a Hilger and Watts four-circle diffractometer.

Crystal Data.—(IVa), $C_9H_9NO_4$, $M = 195.2$, Monoclinic, $a = 5.115(2)$, $b = 10.780(2)$, $c = 16.126(2)$ Å, $\beta = 90.38(2)°$, $U = 889$ Å^3, $D_c = 1.458$, $Z = 4$, $F(000) = 408$. $\lambda(\text{Cu-}K_\alpha) = 1.541\,8$ Å, $\mu(\text{Cu-}K_\alpha) = 10$ cm^{-1}. Space group $P2_1/c$ (C_{2h}^5) from systematic absences: $h0l$ with l odd, $0k0$ with k odd.

(IVb), $C_{19}H_{13}NO_4$, $M = 319.3$, Monoclinic, $a = 14.241(2)$, $b = 7.441(1)$, $c = 19.433(2)$ Å, $\beta = 131.49(1)°$, $U = 1\,543$ Å^3, $D_c = 1.374$, $Z = 4$, $F(000) = 664$. $\mu(\text{Cu-}K_\alpha) = 8.2$ cm^{-1}. Space group $P2_1/c$ (C_{2h}^5) from systematic absences: $h0l$ with l odd, $0k0$ with k odd.

The crystal of (IVa) was a pale yellow needle (0.7 × 0.2 × 0.16 mm) elongated along c while that of (IVb) was a yellow prism (0.7 × 0.3 × 0.15 mm) elongated along c with {010} well developed. Intensity measurements for each compound were made by use of nickel-filtered Cu-K_α radiation on a Hilger and Watts Y 290 four-circle diffractometer controlled by a PDP 8I computer, and equipped with scintillation counter and pulse-height analyser. Data were collected in 70 steps of 0.1° s^{-1} for 2θ 0—146° (IVa) and 0—114° (IVb). During each data collection the intensities of two reference reflections monitored every 50 measurement cycles showed no significant variation. 1 645 reflections were obtained for (IVa) of which 1 226 had $I > 3\sigma(I)$; for (IVb) values are 2 011 and 1 690.

Structure Determination and Refinement.—(*i*) (IVa). The structure was solved by direct methods by use of the Σ_2 and phase routines of the system of crystallographic programs of ref. 4. Data were placed on an absolute scale by Wilson's method,[5] and normalized structure amplitudes E, were derived. Three reflections were assigned phases of zero degrees to fix the origin. From the 199 E values >1.5, 152 were assigned phases, 69 with zero phases and 83 with phases of 180°. An E map calculated with these 152 reflection data as coefficients revealed all 14 non-hydrogen atom positions.

Initial refinement with isotropic thermal parameters (and scattering factors of ref. 6*a* for non-hydrogen and 6*b* for hydrogen atoms) was by full-matrix least-squares calculations. Subsequent anisotropic refinement was by block-diagonal least-squares and three cycles reduced R to 0.076. A three-dimensional difference synthesis computed at this stage revealed the positions of all 9 hydrogen atoms. These were included in the refinement with isotropic thermal parameters. Three further cycles of refinement gave a final R of 0.044 for the 1 226 observed reflections and 0.050 for all 1 645 reflections. The final value for the weighted factor R' $\{[\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}\}$ for observed data was 0.056. The weighting scheme adopted had the form $\sqrt{w} = 1/[\sigma^2(F) + pF^2]^{1/2}$ where the final p parameter was 2.5×10^{-3}. The relative validity of the weighting scheme, as judged by the variation of the average of $w\Delta^2$ with $\sin\theta/\lambda$ and (F_o), was satisfactory. The maximum ratio of shift-to-σ in the final cycle of refinement was 0.5.

(*ii*) (IVb). Data were placed on an absolute scale as before,[5] and normalized structure amplitudes E derived. Three reflections were assigned phases of zero degrees to fix the origin. Preliminary phasing by hand yielded phases for 28 of the 32 reflections with largest E values. These 28 phased reflections were subsequently used as input in the tangent formula.[7] Additional reflections whose phases were unknown were added in order of decreasing E. Of 304 E values >1.5, 151 were assigned phases of zero and 153 phases of 180°. An E map calculated with these 304 reflection data as coefficients revealed all 24 non-hydrogen atom positions.

The structure was initially refined by full-matrix least-squares methods with the scattering factors of ref. 6*c*, isotropic thermal parameters, and weights, w, set at zero, for unobserved reflections and for observed reflections, set equal to the reciprocal of the variance in F as determined from counting statistics. Three cycles of refinement reduced R from 0.281 to 0.121. Subsequent anisotropic refinement by block-diagonal least-squares methods reduced R after four cycles to 0.081. A three-dimensional difference synthesis then clearly revealed all 13 hydrogen atom positions. These were then included in the refinement with isotropic thermal parameters and the scattering curve of ref. 6*b*. Three further cycles of refinement gave R 0.039 for observed and 0.054 for all reflections. The final value of R'

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[3] A. N. Campbell-Crawford, A. M. Gorringe, and D. Lloyd, *Chem. and Ind.*, 1966, 1961.

[4] *X*-Ray System of Computing Programs, Computing Science Center, University of Maryland, College Park, Maryland, Reports TR 67 58 (1970 revision) and TR 192, 1972.

[5] A. J. C. Wilson, *Nature*, 1942, **150**, 151.

[6] (*a*) D. Cromer and J. Mann, *Acta Cryst.* 1968, **A24**, 321; (*b*) R. F. Stewart, F. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175; (*c*) 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[7] J. Karle and H. Hauptman, *Acta Cryst.*, 1956, **9**, 635.

for observed data was 0.055. The maximum ratio of shift-to-σ in the final cycle of refinement was 0.6.

RESULTS

Views produced by ORTEP[8] of the molecular structures of both derivatives are shown in Figures 1 and 2, together with the crystallographic numbering scheme. Molecular packing diagrams are given in Figures 3 and 4. Final positional parameters for non-hydrogen atoms are listed in Tables 1, and positional and thermal parameters for hydrogen atoms in Table 2. Interatomic distances and angles are given in Table 3. Details of mean molecular plane calculations, thermal parameters of non-hydrogen atoms, and measured and calculated structure amplitudes for both (IVa) and (IVb) are listed in Supplementary Publication No. SUP 21314 (22 pp., 1 microfiche).*

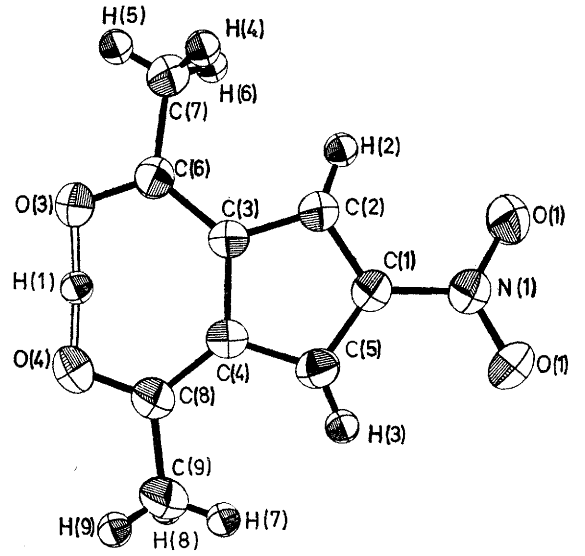

FIGURE 1 Diagram of (IVa); thermal ellipsoids are at 50% probability level

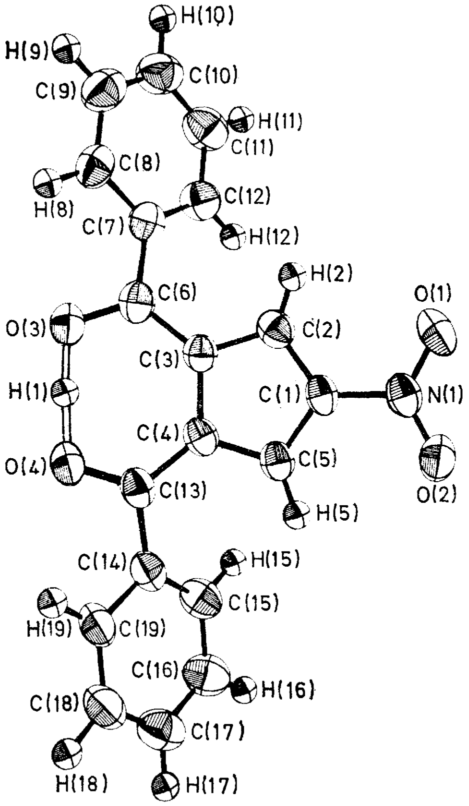

FIGURE 2 Diagram of (IVb)

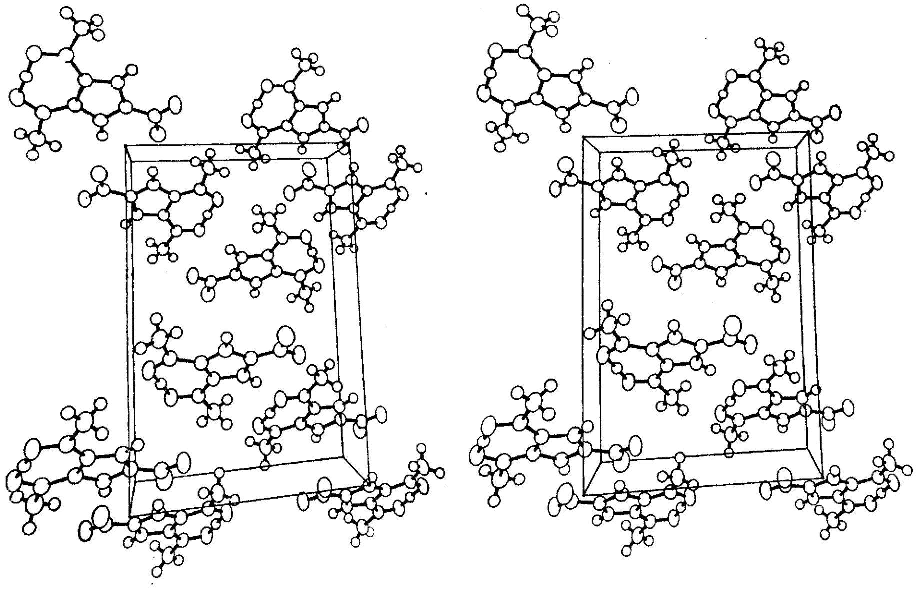

FIGURE 3 Stereodiagram of the molecular packing of (IVa)

DISCUSSION

There has been much discussion concerning the structures of β-ketoenols and their vinylogues, *i.e.* whether

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue.

[8] C. K. Johnson, ORTEP, 1965, Report ORNL 3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

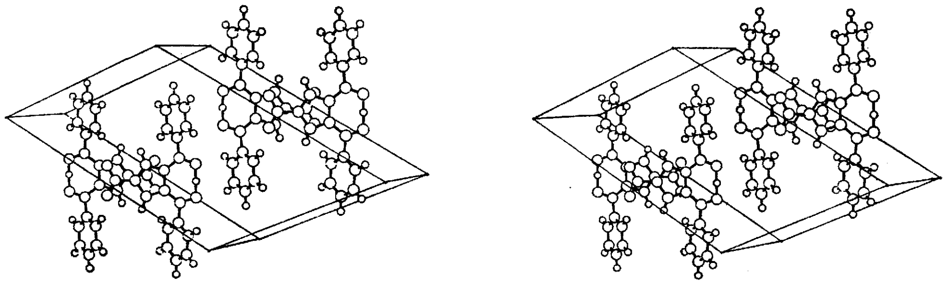


FIGURE 4 Stereodiagram of the molecular packing of (IVb)

TABLE 1

Final positional parameters (× 10^4) for non-hydrogen atoms

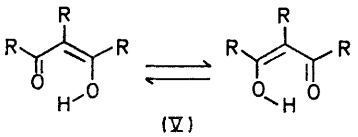
Atom	*x*	*y*	*z*
(*a*) (IVa)			
N(1)	−1 509(4)	6 248(2)	4 049(1)
O(1)	−0 244(3)	7 142(1)	3 809(1)
O(2)	−3 497(4)	6 351(2)	4 465(1)
O(3)	3 805(3)	1 709(1)	2 748(1)
O(4)	0 600(3)	0 817(1)	3 696(1)
C(1)	−0 621(4)	5 027(2)	3 843(1)
C(2)	1 403(4)	4 777(2)	3 294(1)
C(3)	1 671(4)	3 494(2)	3 259(1)
C(4)	−0 266(4)	2 954(2)	3 819(1)
C(5)	−1 672(4)	3 943(2)	4 161(1)
C(6)	3 504(4)	2 875(2)	2 739(1)
C(7)	5 173(5)	3 575(2)	2 149(2)
C(8)	−0 721(4)	1 693(2)	4 018(1)
C(9)	−2 740(5)	1 302(2)	4 626(2)
(*b*) (IVb)			
N(1)	0 093(1)	2 348(2)	5 002(1)
O(1)	1 209(1)	1 945(2)	5 566(1)
O(2)	−0 597(1)	1 986(2)	4 179(1)
O(3)	−1 158(1)	5 676(2)	7 115(1)
O(4)	−3 182(1)	5 690(2)	5 555(1)
C(1)	−0 434(2)	3 301(2)	5 319(1)
C(2)	0 220(2)	3 774(3)	6 230(1)
C(3)	−0 623(2)	4 633(2)	6 261(1)
C(4)	−1 842(2)	4 661(2)	5 321(1)
C(5)	−1 682(2)	3 836(2)	4 756(1)
C(6)	−0 317(2)	5 235(3)	7 087(1)
C(7)	0 989(2)	5 361(3)	7 965(1)
C(8)	1 248(2)	4 838(3)	8 768(1)
C(9)	2 465(2)	4 948(3)	9 602(1)
C(10)	3 409(2)	5 617(3)	9 653(1)
C(11)	3 149(2)	6 183(3)	8 864(2)
C(12)	1 942(2)	6 045(3)	8 016(1)
C(13)	−3 023(2)	5 251(3)	5 000(1)
C(14)	−4 153(2)	5 334(3)	4 013(1)
C(15)	−4 135(2)	6 047(3)	3 363(1)
C(16)	−5 231(2)	6 141(3)	2 448(1)
C(17)	−6 338(2)	5 506(3)	2 183(1)
C(18)	−6 371(2)	4 812(3)	2 826(2)
C(19)	−5 288(2)	4 733(3)	3 743(1)

TABLE 2

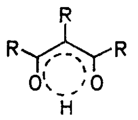
Final positional parameters (× 10^3) and isotropic thermal parameters (× 10^2Å^2) for hydrogen atoms

Atom	*x*	*y*	*z*	*U*
(*a*) (IVa)				
H(1)	219(7)	129(3)	323(2)	9.1(11)
H(2)	249(5)	539(3)	302(2)	5.9(7)
H(3)	−303(5)	395(2)	453(2)	4.6(7)
H(4)	417(8)	410(4)	182(3)	10.6(12)
H(5)	608(9)	307(5)	185(3)	13.4(16)
H(6)	603(8)	422(4)	241(3)	11.4(14)
H(7)	−387(7)	195(4)	479(2)	9.8(11)
H(8)	−196(8)	118(4)	514(3)	11.2(13)
H(9)	−352(8)	057(4)	445(3)	12.2(14)
(*b*)(IVb)				
H(1)	−218(2)	561(3)	637(1)	12.4(8)
H(2)	107(2)	349(3)	675(1)	6.8(6)
H(5)	−233(2)	362(3)	409(1)	7.3(6)
H(8)	052(2)	440(3)	873(1)	9.6(7)
H(9)	261(2)	450(3)	1 015(1)	11.3(8)
H(10)	431(2)	576(3)	1 029(1)	10.1(7)
H(11)	379(2)	671(3)	887(1)	10.8(7)
H(12)	176(2)	641(3)	746(1)	9.5(7)
H(15)	−332(2)	653(3)	356(1)	7.7(6)
H(16)	−518(2)	676(3)	198(1)	10.0(7)
H(17)	−712(2)	558(3)	153(1)	9.2(7)
H(18)	−721(2)	434(3)	260(1)	11.5(8)
H(19)	−529(2)	421(3)	423(1)	10.9(8)

the enol proton is engaged in a rapid tautomeric equilibrium (V) or is located midway between the oxygen atoms (VI). In the case of the enol form of dibenzoylmethane, an *X*-ray diffraction study indicates that the molecule is not symmetrical, *i.e.* it is a ketoenol,[9] whereas a similar study on 1,1,2,2-tetra-acetylethane (a bisacetylacetone) indicates that the ketoenol moieties are symmetric as in (VI).[10] In tropolone, which is isoelectronic with 2-acyl-6-hydroxyfulvenes, adjacent molecules are hydrogen bonded as dimers, in a similar fashion to carboxylic acids, and there are significant differences in the two C–O bond lengths in each molecule.[11] In none of these examples were the hydrogen atoms located and symmetry was judged by the equivalence or non-equivalence of the C–O and C–C bond lengths. The mean O · · · H · · · O distance in the β-ketoenols was *ca.* 2.44 Å.[9-11]



(V)



(VI)

A recent determination [12] of the microwave spectrum of (VII) and of its deuteriated form puts a lower limit of 2 × 10^{12} s^{-1} for any rate of tautomerism between the

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[9] D. E. Williams, *Acta Cryst.*, 1966, **21**, 340.

[10] J. P. Schaefer and P. J. Wheatley, *J. Chem. Soc.* (*A*), **1966**, 528.

[11] H. Shimanouchi and Y. Sasada, *Tetrahedron Letters*, 1970, 2421.

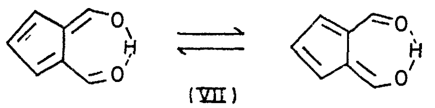
[12] H. M. Pickett, *J. Amer. Chem. Soc.*, 1973, **95**, 1970.

Table 3

Selected intramolecular distances (Å) and bond angles (°)

(*a*) (IVa)			
(i) Distances			
N(1)–O(1)	1.225(3)	C(3)–C(6)	1.427(3)
N(1)–O(2)	1.227(3)	C(4)–C(8)	1.417(3)
		C(6)–C(7)	1.489(3)
N(1)–C(1)	1.432(3)	C(8)–C(9)	1.490(4)
O(3)–C(6)	1.267(3)	H(1)–O(3)	1.23(3)
O(4)–C(8)	1.273(3)	H(1)–O(4)	1.22(3)
		H(2)–C(2)	0.97(3)
O(3) · · · O(4)	2.446(2)	H(3)–C(5)	0.92(2)
		H(4)–C(7)	0.93(4)
C(1)–C(2)	1.393(3)	H(5)–C(7)	0.87(5)
C(1)–C(5)	1.386(3)	H(6)–C(7)	0.92(4)
C(2)–C(3)	1.391(3)	H(7)–C(9)	0.95(4)
C(3)–C(4)	1.466(3)	H(8)–C(9)	0.93(4)
C(4)–C(5)	1.402(3)	H(9)–C(9)	0.93(5)
(ii) Angles			
O(3)–H(1)–O(4)	177(3)	C(4)–C(3)–C(6)	128.7(2)
		C(3)–C(4)–C(5)	106.9(2)
O(1)–N(1)–O(2)	122.9(2)	C(3)–C(4)–C(8)	129.4(2)
O(1)–N(1)–C(1)	118.7(2)	C(5)–C(4)–C(8)	123.7(2)
O(2)–N(1)–C(1)	118.4(2)	C(1)–C(5)–C(4)	107.1(2)
		C(3)–C(6)–C(7)	121.3(2)
N(1)–C(1)–C(2)	124.3(2)	C(3)–C(6)–O(3)	122.5(2)
N(1)–C(1)–C(5)	124.4(2)	C(7)–C(6)–O(3)	116.2(2)
C(2)–C(1)–C(5)	111.3(2)	C(4)–C(8)–O(4)	122.0(2)
C(1)–C(2)–C(3)	107.0(2)	C(4)–C(8)–C(9)	122.5(2)
C(2)–C(3)–C(6)	123.7(2)	C(9)–C(8)–O(4)	115.5(2)
C(2)–C(3)–C(4)	107.6(2)		
(*b*) (IVb)			
(i) Distances			
N(1)–O(1)	1.230(2)	C(14)–C(15)	1.387(5)
N(1)–O(2)	1.230(2)	C(14)–C(19)	1.402(4)
		C(15)–C(16)	1.388(3)
N(1)–C(1)	1.433(4)	C(16)–C(17)	1.377(4)
O(3) · · · O(4)	2.433(2)	C(17)–C(18)	1.382(5)
O(3)–C(6)	1.277(4)	C(18)–C(19)	1.385(3)
O(4)–C(13)	1.282(4)		
		H(1)–O(3)	1.19(3)
C(1)–C(2)	1.395(3)	H(1)–O(4)	1.25(3)
C(1)–C(5)	1.393(3)		
C(2)–C(3)	1.396(4)	H(2)–C(2)	0.96(2)
C(3)–C(4)	1.467(2)	H(5)–C(5)	1.00(2)
C(3)–C(6)	1.428(4)	H(8)–C(8)	1.05(4)
C(4)–C(5)	1.401(4)	H(9)–C(9)	1.00(4)
C(4)–C(13)	1.422(4)	H(10)–C(10)	1.06(2)
C(6)–C(7)	1.475(2)	H(11)–C(11)	1.00(4)
C(7)–C(8)	1.401(4)	H(12)–C(12)	0.98(3)
C(7)–C(12)	1.388(4)	H(15)–C(15)	1.03(3)
C(8)–C(9)	1.386(3)	H(16)–C(16)	1.08(4)
C(9)–C(10)	1.375(5)	H(17)–C(17)	1.00(2)
C(10)–C(11)	1.384(5)	H(18)–C(18)	1.04(3)
C(11)–C(12)	1.389(3)	H(19)–C(19)	1.04(4)
C(13)–C(14)	1.478(2)		
(ii) Angles			
O(3)–H(1)–O(4)	172(3)	C(6)–C(7)–C(8)	118.0(3)
O(1)–N(1)–O(2)	123.6(3)	C(6)–C(7)–C(12)	122.0(2)
O(1)–N(1)–C(1)	118.2(2)	C(8)–C(7)–C(12)	120.0(2)
O(2)–N(1)–C(1)	118.2(2)	C(7)–C(8)–C(9)	119.2(3)
		C(8)–C(9)–C(10)	120.8(3)
N(1)–C(1)–C(2)	124.8(2)	C(9)–C(10)–C(11)	120.0(2)
N(1)–C(1)–C(5)	124.1(2)	C(10)–C(11)–C(12)	120.2(3)
C(2)–C(1)–C(5)	111.0(3)	C(7)–C(12)–C(11)	119.7(3)
C(1)–C(2)–C(3)	107.4(2)	O(4)–C(13)–C(4)	121.7(2)
C(2)–C(3)–C(4)	107.2(2)	O(4)–C(13)–C(14)	115.7(2)
C(2)–C(3)–C(6)	124.1(2)	C(4)–C(13)–C(14)	122.5(3)
C(4)–C(3)–C(6)	128.5(2)	C(13)–C(14)–C(15)	122.5(2)
C(3)–C(4)–C(5)	107.3(2)	C(13)–C(14)–C(19)	117.8(3)
C(3)–C(4)–C(13)	129.2(3)	C(15)–C(14)–C(19)	119.6(2)
C(5)–C(4)–C(13)	123.4(2)	C(14)–C(15)–C(16)	120.1(3)
C(1)–C(5)–C(4)	107.1(2)	C(15)–C(16)–C(17)	120.0(3)
O(3)–C(6)–C(3)	122.1(2)	C(16)–C(17)–C(18)	120.4(2)
O(3)–C(6)–C(7)	115.8(2)	C(17)–C(18)–C(19)	120.2(3)
C(3)–C(6)–C(7)	122.1(3)	C(14)–C(19)–C(18)	119.6(3)

two prototropic forms; the data were consistent with C_{2v} symmetry and it was difficult to see how the barrier to interconversion could extend much above ground vibrational level.



(VII)

The present *X*-ray studies confirm that in the solid-state the structure of 2,3-diacyl-5-nitrocyclopentadiene is a symmetric delocalized one (IV) similar to that inferred from the n.m.r. spectra.[2] The enolic hydrogen H(1) has been clearly resolved and is midway between the two carbonyl oxygen atoms [O(3) · · · O(4) 2.433(2) in (IVb), and 2.446(2) Å (IVa)]. In the (IVa) derivative, the O · · · H distances (mean 1.22 Å) are essentially identical (Table 4). In (IVb), the hydrogen appears closer to O(3) by 0.06 Å (2σ) but consideration of the C–C and C–O bond lengths shows no asymmetry and thus the apparent difference in O · · · H distances is probably not significant.

With this assumption, examination of Figures 1 and 2 reveals the presence of approximate mirror symmetry through N(1), C(1), and H(1). The mean C(3)–C(4) bond length (1.467 Å) is similar in length to a C–C single bond in cyclo-octatetraene [13] (1.462 Å) whereas the remaining C–C bonds in the five membered ring are all similar (1.392—1.402, mean 1.396 Å for both derivatives), and close to that found in benzene.[14] The C(3)–C(6) and C(4)–C(8Me,13Ph) bond lengths (mean 1.425 Å) are much shorter than the accepted value (1.506 Å) for C–C adjacent to carbonyl,[13] while the mean bond length for C(6)–O(3) and C(8Me,13Ph)–O(4) (1.275 Å) is substantially greater than for a normal C=O bond, 1.215 Å.[13] It therefore appears that there is a delocalized system extending through O(3), C(6), C(3), C(2), C(1), C(5), C(4), C(8Me,13Ph), O(4), and H(1). There are ten π electrons available and it is tempting to infer the presence of a delocalized π system making the molecule structurally similar to azulene.[15] A series of INDO/2 (intermediate neglect of differential overlap) and CNDO/2 (complete neglect of differential overlap) calculations were carried out for each compound in order to obtain π bond-orders and π electron-densities at all atoms involved in delocalization. To simplify the calculations in the case of (IVa), the methyl groups, not being involved in the delocalization, were replaced by hydrogens. In (IVb) the phenyl rings are not involved in conjugation [the phenyl rings are rotated by *ca.* 50° to the plane of the molecule and the C(6)–C(7) and C(13)–C(14) bond lengths (mean 1.476 Å) do not differ from the expected value for a C(sp^2)–C(sp^2) (1.47 Å) [13]] and were likewise replaced by hydrogens to simplify the calculations. The results are summarized in Figures 5 and 6. The most noteworthy features are the

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[13] *Chem. Soc. Special Publ.*, No. 18, 1965.

[14] G. E. Bacon, N. A. Cuniry, and S. A. Wilson, *Proc. Roy. Soc.* (*A*), 1964, **279**, 98.

[15] J. M. Robertson, H. M. M. Shearer, G. A. Sim, and D. G. Watson, *Acta Cryst.*, 1961, **15**, 1; G. S. Pawley, *ibid.*, 1965, **18**, 560.

equal π electron-densities on O(3) and O(4), and the π bond-orders. In the cyclopentadiene ring, except for the C(3)–C(4) bond, these bond orders are all similar to that (0.67) for benzene. The other values are consistent with the presence of a delocalized π-system. In addition, the calculated electron density at H(1) (mean 0.68) is consistent with the observed signal at very low field in the n.m.r. spectrum (−9.35 τ).[3]

In both structures the NO_2 groups are nearly co-planar with the cyclo-pentadiene rings; the dihedral angle being 8.6 (IVa) and 1.5° (IVb). The mean N–C bond length [1.433(4) Å] is *ca.* 0.03 Å shorter than that in nitromethane [1.46(2) Å],[16] where no conjugation occurs. The mean π bond-order for this bond is 0.27 (Figures 5 and 6) but the amount of conjugation must be fairly small since the calculations show a maximum barrier to rotation of *ca.* 3 kcal., a value similar in magnitude to that for ethane.[17] Packing considerations are also probably of some importance in the near co-planarity of the nitro-groups and cyclopentadiene rings.

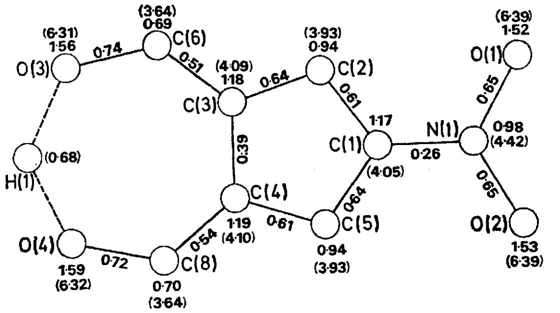

FIGURE 5 Results of INDO/2 calculations for (IVa). Numbers along the bond represent π bond-orders. The two additional numbers given at each atom [except H(1)] are (in parentheses) total number of valence electrons (*i.e.* excluding 1*s* for C, N, and O), and (not in parentheses) π electron density

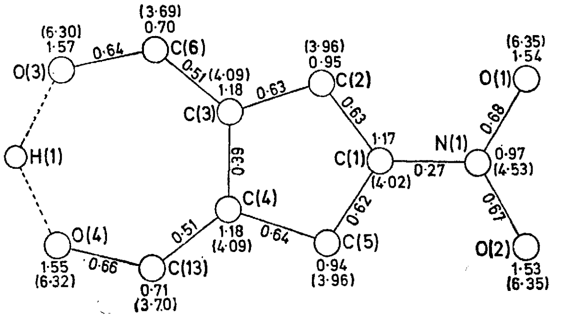

FIGURE 6 Results of CNDO/2 calculations for (IVb). See caption to Figure 5 for definition of numbers

Packing.—The molecules of (IVb) are arranged in stacks parallel to *b* with neighbouring molecules in the stack related to one another through inversion centres (Figure 4). The arrangement is such that the nitro-group and cyclopentadiene ring of one molecule are sandwiched almost exactly between those of the two neighbouring molecules in the stack. The two independent distances between molecular planes in the stack are 3.18 and 3.33 Å. Individual intermolecular distances are listed in Table 4(*a*). The molecular packing arrangement in (IVa) derivative is somewhat more complex (Figure 3). There is no continuous stacking of molecules as in (IVb): discrete pairs of molecules, related through one set of inversion centres at 0,0,0, *etc.*, have an interplanar spacing of 3.32 Å but the extent of the overlap between the nitro-group of one molecule and the five-membered ring of the other is less than that for (IVb). There are in addition small amounts of overlap between the nitro-group of one molecule and the seven-membered ring of molecules related by two-fold screw axes; pertinent distances are in Table 4. Operation of the other independent set of inversion centres at 1/2,0,0, *etc.* leads to essentially planar pairs of molecules with the shortest intermolecular contacts ' in plane ' between nitro-oxygen O(2) and hydrogen atoms H(3) on C(5) and H(7) on C(9) (Table 4). These types of packing have been found in crystals of charge-transfer complexes and this effect may also occur in (IVa) and (IVb) although to a rather limited extent since the colours of the crystals are not intense and the intermolecular distances approach van der Waals values. Shorter remaining intermolecular distances (Table 4) are mainly between hydrogen and oxygen atoms and correspond to van der Waals interactions.

TABLE 4

Intermolecular distances (Å)

(*a*) Interplanar contacts			
(i) (IVb)			
N(1) ··· C(1^{I})	3.392(2)	O(2) ··· C(3^{I})	3.471(3)
N(1) ··· C(2^{I})	3.584(3)	C(1) ··· C(1^{I})	3.390(3)
N(1) ··· C(4^{I})	3.691(3)	N(1) ··· N(1^{II})	3.504(2)
N(1) ··· C(5^{I})	3.463(3)	N(1) ··· O(1^{II})	3.486(2)
O(1) ··· C(4^{I})	3.496(3)	N(1) ··· O(2^{II})	3.455(2)
O(1) ··· C(5^{I})	3.356(2)	O(1) ··· O(2^{II})	3.183(2)
O(2) ··· C(2^{I})	3.382(3)		
(ii) (IVa)			
N(1) ··· C(4^{I})	3.653(2)	O(1) ··· O(3^{III})	3.127(2)
N(1) ··· C(5^{I})	3.311(2)	O(1) ··· C(6^{III})	3.095(2)
O(2) ··· C(4^{I})	3.443(3)	O(2) ··· O(3^{III})	3.592(2)
O(2) ··· C(5^{I})	3.453(3)	C(1) ··· O(3^{III})	3.531(2)
N(1) ··· O(3^{III})	3.159(2)	C(2) ··· O(4^{III})	3.544(2)
N(1) ··· C(6^{III})	3.520(3)		
(*b*) Other molecular contacts			
(i) (IVb)			
O(2) ··· H(12^{I})	2.71(2)	O(1) ··· H(17^{V})	2.61(2)
O(2) ··· H(15^{I})	2.54(2)	H(8) ··· O(2^{VI})	2.49(3)
H(19) ··· O(4^{IV})	2.47(3)		
(ii) (IVa)			
H(8) ··· O(1^{I})	2.72(4)	H(2) ··· O(3^{VII})	2.68(3)
O(2) ··· H(3^{IV})	2.43(3)	H(6) ··· O(3^{VII})	2.70(4)
H(7) ··· O(2^{IV})	2.58(4)	H(5) ··· O(1^{VIII})	2.59(5)
O(1) ··· H(8^{VII})	2.59(5)		

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

I	$-x, 1-y, 1-z$	V	$1+x, \frac{1}{2}-y, \frac{1}{2}+z$
II	$-x, -y, 1-z$	VI	$x, \frac{1}{2}-y, \frac{1}{2}+z$
III	$-x, \frac{1}{2}+y, \frac{1}{2}-z$	VII	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$
IV	$-1-x, 1-y, 1-z$	VIII	$1-x, y-\frac{1}{2}, \frac{1}{2}-z$

These structures may be compared with that obtained by crystallographic examination [18] of the aza-analogue

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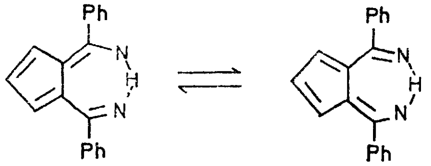
[16] *Chem. Soc. Special Publ.*, No. 11, 1958.

[17] L. Pauling, ' The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960.

[18] H. L. Ammon and U. Mueller-Westerhoff, *Tetrahedron*, 1974, **30**, 1437.



(VIII)

(VIII), which indicated that this molecule, unlike the present oxa-compounds, is not symmetrical, and exists in defined equilibrating prototropic forms. The difference between the oxa- and aza-compounds may be due to the greater electronegativity of oxygen atoms *vis à vis* nitrogen atoms. This is also reflected by the n.m.r. signals for the enolic proton of (IVa) [τ −9.35 ($CDCl_3$)], and those of a number of 2-acyl-6-hydroxyfulvenes [τ −8.0 to −9.35 (CCl_4 or $CDCl_3$)] [2] compared to the amino proton of (VIII) [τ −5.73 (CCl_4)].[19]

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[4/2292 *Received, 5th November,* 1974]

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[19] U. Mueller-Westerhoff, *J. Amer. Chem. Soc.*, 1970, **92**, 4849.