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9-(Cyclohepta-2,4,6-trien-1-yl)xanthen-9-ol. X-ray Crystal Structure and Computationally Optimized Structures Compared

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Abstract. The structure of the title compound (1) has been determined experimentally from X-ray data. This is compared with optimized structures computed with semi-empirical molecular orbital (*MNDO*, *AM1*, *PM3*) and molecular mechanics methods. $C_{20}H_{16}O_2$, $M_r = 288.35$, monoclinic, $P2_1/n$, $a = 12.690$ (3), $b = 6.140$ (1), $c = 19.660$ (4) Å, $\beta = 106.74$ (2)°, $V = 1466.9$ Å³, $Z = 4$, $D_x = 1.31$ g cm⁻³, Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å, $\mu = 0.8$ cm⁻¹, $F(000) = 608$, $T = 294$ (1) K, $R = 0.047$ for 1725 unique observed reflections. Although the molecules in the solid-state structure are linked by hydrogen bonds, there is little difference between the calculated gas-phase structures and that observed in the crystal.

Introduction. We have recently reported the synthesis of 9-(cyclohepta-2,4,6-trien-1-yl)xanthen-9-ol (1) (Badejo, Karaman, Lee, Lutz, Mamanta & Fry, 1989), together with some of its interesting chemical behavior (Badejo, Karaman & Fry, 1989; Karaman, Badejo & Fry, 1989). We have now determined its structure from both a single-crystal X-ray diffraction

study and from computations using semi-empirical molecular orbital and molecular mechanics energy-minimized methods.

Experimental.

X-ray

The title compound was obtained as pale-yellow elongated plates from THF/pentane. A crystal having approximate dimensions of 0.25 × 0.20 × 0.10 mm was mounted in a glass capillary. Preliminary examination and data collection were performed with Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) on an Enraf–Nonius CAD-4 diffractometer. Cell constants were obtained from the setting angles of 25 reflections in the range $9 < \theta < 15^\circ$. As a check on crystal quality, ω -scans of several intense reflections were measured; the width at half-height was 0.20° indicating good crystal quality. From the systematic absences of $h0l$ $h+l = 2n+1$, $0k0$ $k = 2n+1$ the space group was determined to be $P2_1/n$. Data were collected ($\omega-2\theta$ scans) to a maximum 2θ of 60.0°.

$0 \leq h \leq 17$, $0 \leq k \leq 8$, $-27 \leq l \leq 27$. A total of 4823 reflections were collected, 4637 unique ($R_{\text{int}} = 2.2\%$, decay = 0.6%, empirical absorption correction, relative transmission coefficients 0.785 to 0.996). The structure was solved by direct methods, completed by Fourier syntheses and refined by full-matrix least squares where the function minimized was $\sum w(F_o - |F_c|)^2$, $w = 4F_o^2/\sigma^2(F_o^2)$. In the final cycles all non-hydrogen atoms were refined anisotropically and the hydrogen atoms isotropically. $R = 0.047$, $wR = 0.051$, $S = 1.39$ for 263 variables and 1725 reflections with $F_o^2 > 3\sigma(F_o^2)$. $\Delta/\sigma_{\text{max}} = 0.03$, $\Delta\rho_{\text{max}} = 0.20$ (5), $\Delta\rho_{\text{min}} = -0.21$ (5) $e \text{ \AA}^{-3}$. Scattering factors and values for $\Delta f'$ and $\Delta f''$ for non-hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 71–102, 149–150). All calculations were performed on a VAX11/750 computer using *SDP/VAX* (Frenz, 1978). Final atomic parameters are reported in Table 1 and an *ORTEP*II (Johnson, 1971) view of the molecule is shown in Fig. 1.*

Theoretical calculations

The *MNDO*, *AM1* and *PM3* calculations were done using *MOPAC* version 5.0 (QCPE No. 455) running on a CRAY X-MP/28 computer in the Ohio Supercomputer Center. The starting geometries were obtained from the *PCMODEL* program (Serena Software, 1989). The calculations were carried out by the standard *MNDO* (Dewar & Thiel, 1977), *AM1* (Dewar, Zoebisch, Healy & Stewart, 1985) and *PM3* (Stewart, 1989) programs based on the restricted Hartree-Fock (RHF) method. Geometries were optimized in internal coordinates and were terminated when Herberts test was satisfied in the Broyden-Fletcher-Goldfarb-Shanno method (BFGS). All optimizations were terminated when the change in energy on successive iterations was less than $0.00001 \text{ kcal mol}^{-1}$ ($1 \text{ cal} = 4.184 \text{ J}$) and the change in density matrix elements on two successive iterations was less than 0.001. All calculations were performed with full optimization of all geometrical variables (bond lengths, bond angles and dihedral angles) without any symmetry constraint. The molecular mechanics calculation (Burkert & Allinger, 1982) was conducted using the *MMX* program (Serena Software, 1987) on a Zenith 80286/80287 microcomputer. The X-ray coordinates were used as input for this calculation.

Table 1. Positional parameters and their e.s.d.'s

	x	y	z	B(\AA^2)
O10	0.1230 (1)	-0.1362 (3)	0.22146 (8)	2.90 (4)
O15	-0.0142 (1)	0.4852 (3)	0.19049 (9)	3.35 (4)
C1	0.0534 (2)	0.2726 (5)	0.0800 (1)	3.31 (6)
C2	0.1075 (2)	0.1852 (5)	0.0346 (1)	3.85 (6)
C3	0.1638 (2)	-0.0086 (5)	0.0516 (1)	3.72 (6)
C4	0.1678 (2)	-0.1127 (5)	0.1136 (1)	3.22 (6)
C5	0.1411 (2)	-0.1161 (5)	0.3431 (1)	3.27 (6)
C6	0.1235 (2)	-0.0114 (5)	0.4006 (1)	3.88 (6)
C7	0.0663 (2)	0.1825 (6)	0.3918 (1)	3.98 (6)
C8	0.0237 (2)	0.2697 (5)	0.3249 (1)	3.20 (6)
C9	-0.0115 (2)	0.2532 (4)	0.1906 (1)	2.39 (5)
C11	0.0544 (2)	0.1686 (4)	0.1429 (1)	2.42 (5)
C12	0.1137 (2)	-0.0228 (4)	0.1593 (1)	2.46 (5)
C13	0.0378 (2)	0.1661 (4)	0.2651 (1)	2.47 (5)
C14	0.0988 (2)	-0.0243 (4)	0.2762 (1)	2.53 (5)
C16	-0.1539 (2)	-0.0511 (4)	0.1524 (1)	2.63 (5)
C17	-0.2473 (2)	-0.1310 (5)	0.1094 (1)	3.14 (5)
C18	-0.3407 (2)	-0.0021 (5)	0.0713 (1)	3.54 (6)
C19	-0.3720 (2)	0.1852 (5)	0.0950 (1)	3.63 (6)
C20	-0.3202 (2)	0.2867 (5)	0.1615 (1)	3.40 (6)
C21	-0.2121 (2)	0.2812 (4)	0.1947 (1)	2.98 (5)
C22	-0.1334 (2)	0.1886 (4)	0.1578 (1)	2.33 (5)
H1	0.017 (2)	0.413 (4)	0.069 (1)	5.2 (7)*
H2	0.104 (2)	0.260 (4)	-0.008 (1)	4.5 (6)*
H3	0.200 (2)	-0.075 (5)	0.018 (1)	5.6 (7)*
H4	0.205 (2)	-0.248 (3)	0.125 (1)	3.1 (5)*
H5	0.179 (2)	-0.251 (4)	0.348 (1)	4.4 (6)*
H6	0.154 (2)	-0.073 (4)	0.446 (1)	5.1 (7)*
H7	0.059 (2)	0.265 (4)	0.433 (1)	4.9 (7)*
H8	-0.013 (2)	0.410 (4)	0.319 (1)	3.9 (6)*
H15	0.052 (2)	0.549 (5)	0.207 (1)	6.5 (8)*
H16	-0.097 (2)	-0.144 (4)	0.184 (1)	3.5 (6)*
H17	-0.253 (2)	-0.286 (4)	0.106 (1)	4.0 (6)*
H18	-0.390 (2)	-0.066 (5)	0.029 (1)	4.9 (7)*
H19	-0.443 (2)	0.243 (4)	0.067 (1)	4.2 (6)*
H20	-0.367 (2)	0.361 (4)	0.186 (1)	4.4 (6)*
H21	-0.182 (2)	0.335 (4)	0.241 (1)	2.9 (5)*
H22	-0.153 (2)	0.257 (3)	0.108 (1)	2.4 (5)*

* Atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $8\pi^2/3 \times \text{trace of orthogonalized } U \text{ tensor}$.

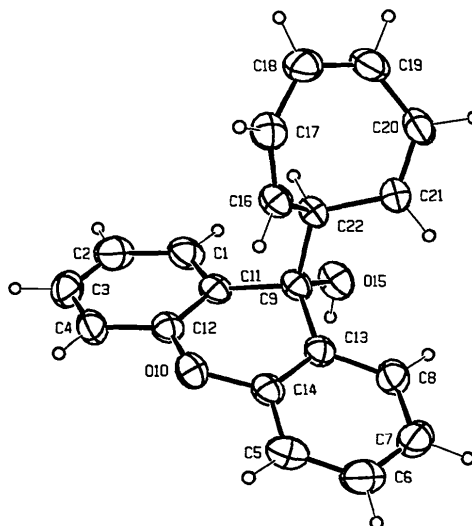


Fig. 1. 9-(Cyclohepta-2,4,6-trien-1-yl)xanthen-9-ol showing atom numbering used and 50% probability ellipsoids.

* Lists of calculated and observed structure factors, anisotropic thermal parameters, distances, angles, torsion angles and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53927 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The structure of the title compound along with the atom numbering is shown in Fig. 1. As expected, the xanthene ring is not planar. The dihedral angle between the two aromatic rings is $21.9(2)^\circ$, both being tipped away from the cyclo-

Table 2. *X-ray and calculated bond distances (Å) for (1)*

Numbers in parentheses are the magnitudes of the differences between the solid-state structure and the calculated one.

X-ray*	MNDO	AM1	PM3	MMX	
O10—C12	1.381	1.366 (15)	1.392 (11)	1.403 (22)	1.367 (14)
O10—C14	1.385	1.382 (3)	1.382 (3)	1.382 (3)	1.368 (17)
O15—C9	1.425	1.408 (17)	1.429 (4)	1.425 (0)	1.422 (3)
C1—C2	1.381	1.378 (3)	1.378 (3)	1.378 (3)	1.399 (18)
C1—C11	1.389	1.417 (28)	1.399 (10)	1.397 (8)	1.405 (16)
C2—C3	1.378	1.406 (28)	1.396 (18)	1.392 (14)	1.400 (22)
C3—C4	1.363	1.400 (37)	1.391 (28)	1.387 (24)	1.397 (34)
C4—C12	1.394	1.421 (27)	1.403 (9)	1.403 (9)	1.405 (11)
C5—C6	1.374	1.364 (10)	1.364 (10)	1.364 (10)	1.396 (22)
C5—C14	1.388	1.423 (35)	1.404 (16)	1.405 (17)	1.405 (17)
C6—C7	1.379	1.407 (28)	1.396 (17)	1.394 (15)	1.399 (20)
C7—C8	1.378	1.403 (25)	1.392 (14)	1.388 (10)	1.399 (21)
C8—C13	1.394	1.417 (23)	1.399 (5)	1.397 (3)	1.406 (12)
C9—C11	1.517	1.550 (33)	1.511 (6)	1.518 (1)	1.519 (2)
C9—C13	1.514	1.549 (35)	1.508 (6)	1.520 (6)	1.518 (4)
C9—C22	1.547	1.605 (58)	1.555 (8)	1.572 (25)	1.554 (7)
C11—C12	1.382	1.424 (42)	1.403 (21)	1.400 (18)	1.405 (23)
C13—C14	1.384	1.424 (40)	1.405 (21)	1.400 (16)	1.408 (24)
C16—C17	1.335	1.335 (0)	1.335 (0)	1.335 (0)	1.352 (17)
C16—C22	1.493	1.516 (23)	1.489 (4)	1.492 (1)	1.505 (12)
C17—C18	1.442	1.459 (17)	1.443 (1)	1.449 (7)	1.463 (21)
C18—C19	1.343	1.357 (14)	1.348 (5)	1.349 (6)	1.358 (15)
C19—C20	1.426	1.461 (35)	1.443 (17)	1.450 (24)	1.463 (37)
C20—C21	1.340	1.355 (15)	1.347 (7)	1.339 (1)	1.352 (12)
C21—C22	1.504	1.515 (11)	1.491 (13)	1.495 (9)	1.506 (2)

* E.s.d.'s on experimental bond distances are 0.003–0.004 Å.

heptatriene substituent. The pyran ring is in the boat conformation, C9 and O10 being 0.315 (3) and 0.194 (2) Å above the C11–C12–C13–C14 plane [maximum deviation 0.003 (3) Å] towards the axial cycloheptatriene substituent. The lower deviation for O10 indicates conjugation of this atom with the two neighboring aromatic rings. The conjugated part of the cycloheptatriene ring is somewhat puckered, with C16, C18, C19 and C21 lying 0.087 (2)–0.107 (3) Å to one side of the least-squares plane, and C17 and C20 0.192 (3)–0.197 (3) Å to the other. C22, of course, lies far [0.930 (2) Å] from this plane. As expected from the structures of similar compounds (Thomas & Coppens, 1972), there is an alternation of short and long bonds in the triene; however, all show multiple bond character.

The molecules are joined together in a head-to-tail manner by fairly long hydrogen bonds. This is indicated by the distance O10—H15 of 2.12 (3) Å and the corresponding angle O10—H15—O15 of 140 (3)°.

The gas-phase structures as calculated by the various methods above are all quite similar and agree closely with the solid-state structure. The observed and calculated distances, bond angles and torsion angles are summarized in Tables 2–4 along with the deviations of the calculated parameters from the experimental ones. The discrepancies, although greater than the experimental errors, are small enough to give us confidence in the computational methods as predictors for geometries of molecules of this type. The average deviations from the experimentally determined structure are quite close for all

Table 3. *X-ray and calculated bond angles (°) for (1)*

Numbers in parentheses are the magnitudes of the differences between the solid-state structure and the calculated one.

X-ray*	MNDO	AM1	PM3	MMX	
C12—O10—C14	117.1	120.4 (3.3)	114.8 (2.3)	116.2 (0.9)	114.1 (3.0)
C2—C1—C11	121.2	121.5 (0.3)	120.3 (1.0)	121.2 (0.0)	121.1 (0.1)
C1—C2—C3	119.9	120.4 (0.5)	120.3 (0.4)	120.3 (0.4)	119.9 (0.0)
C2—C3—C4	120.3	120.2 (0.1)	120.7 (0.4)	120.4 (0.1)	119.5 (0.8)
C3—C4—C12	119.5	119.1 (0.4)	118.6 (0.9)	118.9 (0.6)	120.7 (1.2)
C6—C5—C14	118.6	119.2 (0.6)	118.7 (0.1)	119.2 (0.6)	120.8 (2.2)
C5—C6—C7	120.3	119.9 (0.4)	120.4 (0.1)	120.2 (0.1)	119.3 (0.1)
C6—C7—C8	120.2	120.1 (0.1)	120.2 (0.0)	120.1 (0.1)	120.0 (0.2)
C7—C8—C13	121.2	122.4 (1.2)	120.8 (0.4)	121.2 (0.0)	121.5 (0.3)
O15—C9—C11	111.0	109.7 (1.3)	110.6 (0.4)	110.4 (0.6)	107.2 (3.8)
O15—C9—C13	111.0	109.7 (1.3)	110.6 (0.4)	110.4 (0.6)	109.5 (1.5)
O15—C9—C22	103.6	110.9 (7.3)	109.4 (5.8)	109.7 (6.1)	108.1 (4.5)
C11—C9—C13	109.2	109.9 (0.7)	109.9 (0.7)	109.9 (1.7)	107.5 (1.7)
C11—C9—C22	108.5	113.4 (4.9)	112.7 (4.2)	112.4 (3.9)	109.6 (1.1)
C13—C9—C22	113.5	113.4 (0.1)	112.7 (0.8)	112.4 (1.1)	114.8 (1.3)
C1—C11—C9	121.9	122.5 (0.6)	120.8 (1.1)	121.2 (0.7)	121.0 (0.9)
C1—C11—C12	117.6	116.0 (1.6)	118.0 (0.4)	118.0 (0.4)	118.7 (1.1)
C9—C11—C12	120.4	120.6 (0.2)	120.4 (0.0)	120.5 (0.1)	120.2 (0.2)
O10—C12—C4	116.0	116.0 (0.0)	116.0 (0.0)	114.3 (1.7)	118.4 (2.4)
O10—C12—C11	122.5	122.7 (0.2)	123.1 (0.6)	124.3 (1.8)	121.6 (0.9)
C4—C12—C11	121.5	122.0 (0.5)	121.4 (0.1)	121.4 (0.1)	120.1 (1.4)
C8—C13—C9	122.5	124.0 (1.5)	122.2 (0.3)	121.4 (1.1)	122.1 (0.4)
C8—C13—C14	117.0	116.9 (0.1)	118.8 (1.8)	118.4 (1.4)	118.1 (1.1)
C9—C13—C14	120.5	120.1 (0.4)	119.9 (0.6)	120.6 (0.1)	119.8 (0.7)
O10—C14—C5	115.0	115.0 (0.0)	115.1 (0.1)	114.4 (0.6)	117.8 (2.8)
O10—C14—C13	122.3	122.0 (0.3)	122.5 (0.2)	124.3 (2.0)	121.9 (0.4)
C5—C14—C13	122.7	122.4 (0.3)	121.8 (0.9)	121.3 (1.4)	120.3 (2.4)
C17—C16—C22	120.8	125.3 (4.5)	122.1 (1.3)	121.8 (1.0)	122.4 (1.6)
C16—C17—C18	125.0	127.3 (2.3)	124.9 (0.1)	124.4 (0.6)	125.1 (0.1)
C17—C18—C19	124.8	125.9 (1.1)	126.2 (1.4)	124.8 (0.0)	125.5 (0.7)
C18—C19—C20	126.0	124.6 (1.4)	125.4 (0.6)	125.2 (0.8)	125.6 (0.4)
C19—C20—C21	124.9	126.6 (1.7)	124.7 (0.2)	124.6 (0.3)	125.1 (0.2)
C20—C21—C22	120.3	125.5 (5.2)	122.0 (1.7)	121.1 (0.8)	122.3 (2.0)
C9—C22—C16	114.6	115.2 (0.6)	112.9 (1.7)	112.3 (2.3)	115.2 (0.6)
C9—C22—C21	115.1	117.1 (2.0)	113.5 (1.6)	114.3 (0.8)	114.8 (0.3)
C16—C22—C21	106.3	107.1 (0.8)	109.1 (2.8)	107.6 (1.3)	108.9 (2.6)

* E.s.d.'s on experimental bond angles are 0.2–0.3°.

Table 4. *Selected X-ray and calculated torsion angles (°) for (1)*

Numbers in parentheses are the magnitudes of the differences between the solid-state structure and the calculated one.

X-ray*	MNDO	AM1	PM3	MMX	
C14—O10—C12—C11	-18.1	-15.1 (3.0)	-25.3 (7.2)	-15.2 (2.9)	-33.5 (15.4)
C12—O10—C14—C13	18.8	15.1 (3.7)	24.1 (5.3)	14.0 (4.8)	33.1 (14.3)
C11—C1—C2—C3	-0.1	-0.4 (0.3)	-0.2 (0.1)	-0.4 (0.3)	0.7 (0.8)
C2—C1—C11—C12	1.6	1.5 (0.1)	1.0 (0.6)	0.2 (1.4)	-2.0 (3.6)
C1—C2—C3—C4	-1.0	-0.5 (0.5)	-0.5 (0.5)	0.5 (1.5)	0.6 (1.6)
C3—C4—C12—C11	0.9	0.9 (0.0)	0.3 (0.6)	0.2 (0.7)	-0.8 (1.7)
C14—C5—C6—C7	-0.9	-0.5 (0.4)	-1.3 (0.4)	-0.7 (0.2)	-0.0 (0.9)
C6—C5—C14—C13	-1.3	-2.0 (0.7)	-1.4 (0.1)	-1.1 (0.2)	-0.1 (1.2)
C5—C6—C7—C8	1.8	1.3 (0.5)	1.6 (0.2)	1.3 (0.5)	-0.1 (1.9)
C6—C7—C8—C13	-0.5	0.3 (0.8)	0.9 (1.4)	0.0 (0.5)	0.3 (0.8)
C7—C8—C13—C14	-1.6	-2.7 (1.1)	-3.6 (2.0)	-1.8 (0.2)	-0.3 (1.3)
O15—C9—C11—C12	147.7	135.2 (12.5)	142.2 (5.5)	132.7 (15.0)	144.0 (3.7)
C13—C9—C11—C12	25.0	17.5 (7.5)	22.7 (2.3)	13.3 (11.7)	26.4 (1.4)
C22—C9—C11—C1	77.6	72.6 (5.0)	79.2 (1.6)	69.8 (7.8)	79.2 (1.6)
O15—C9—C13—C14	-147.1	-132.0 (15.1)	-140.4 (6.7)	-130.6 (16.5)	-142.8 (4.3)
C11—C9—C13—C8	156.3	161.4 (5.1)	154.5 (1.8)	165.3 (9.0)	152.7 (3.6)
C22—C9—C13—C8	-82.5	-77.7 (4.8)	-84.8 (2.3)	-73.8 (8.7)	-85.1 (2.6)
C11—C9—C22—C16	62.6	59.7 (2.9)	60.5 (2.1)	64.5 (1.9)	63.7 (1.1)
C13—C9—C22—C16	-59.0	-62.4 (3.4)	-61.2 (2.2)	-58.1 (0.9)	-57.4 (1.6)
C1—C11—C12—O10	-178.0	-178.3 (0.3)	-178.8 (0.8)	-179.0 (1.0)	-176.3 (1.7)
C9—C11—C12—O10	-5.1	-2.4 (2.7)	1.2 (6.3)	1.0 (6.1)	2.4 (7.5)
C9—C13—C14—O10	3.9	2.6 (1.3)	1.4 (2.5)	1.3 (2.6)	-1.6 (5.5)
C22—C16—C17—C18	-7.5	-6.4 (1.1)	-4.1 (3.4)	-1.6 (5.9)	-5.8 (1.7)
C17—C16—C22—C21	69.4	58.5 (10.9)	63.8 (5.6)	65.1 (4.3)	64.7 (4.7)
C16—C17—C18—C19	-33.0	-27.3 (5.7)	-32.6 (0.4)	-37.0 (4.0)	-32.8 (0.2)
C17—C18—C19—C20	-0.9	-3.9 (3.0)	-1.9 (1.0)	-0.1 (0.8)	0.1 (1.0)
C18—C19—C20—C21	33.5	30.9 (2.6)	33.1 (0.4)	34.0 (0.5)	32.8 (0.7)
C19—C20—C21—C22	8.4	9.2 (0.8)	7.7 (0.7)	7.8 (0.6)	5.6 (2.8)
C20—C21—C22—C16	-70.0	-61.3 (8.7)	-66.6 (3.4)	-68.7 (1.3)	-64.6 (5.4)

* E.s.d.'s on experimental torsion angles are 0.2–0.4°.

methods; however, of the semi-empirical methods, *MNDO* gave less satisfactory agreement for the bond lengths. We also note that molecular mechanics methods may give false minima as we have previously shown for this type of molecule (Badejo, Karaman, Pinkerton & Fry, 1990), hence the current *MMX* calculations use the solid-state structure as input to give results for comparison purposes only. The most important differences between the solid-state structure and the calculated ones concern the geometry associated with C9. This is perhaps not unexpected as the hydroxyl group, O15, attached to C9 is involved in hydrogen bonding in the solid (see above) which would be expected to perturb the geometry at C9 compared to the calculated gas-phase structures. The discrepancies relating to the geometry at O10 may also be interpreted in this way; however, there is certainly a contribution from the poor treatment of conjugated systems inherent in the molecular mechanics calculations. All of the calculations showed the energy minimum to be rather flat with respect to the conformation of the seven-membered ring, thus the discrepancies and the variation in the discrepancies for the torsion angles in this ring may be attributed to packing forces and/or uncertainties in the theoretical values.

All methods of calculation give similar heats of formation and dipole moments (Table 5). The weakness of the hydrogen bond is manifested in the similarity of the heat of formation calculated for the X-ray structure compared to that for the gas-phase molecule.

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Table 5. *Heats of formation and dipole moments calculated for (1)*

Geometry	<i>MNDO</i>	<i>AM1</i>	<i>PM3</i>	<i>MMX</i>
Gas-phase optimized				
ΔH_f° (kcal mol ⁻¹)*	28.2	33.9	29.7	28.3
μ (D)‡	1.41	1.27	1.39	1.85
X-ray optimized†				
ΔH_f° (kcal mol ⁻¹)*	30.3	34.5	30.9	
μ (D)‡	1.43	1.40	1.32	

* 1 cal = 4.184 J.

† Optimization of the X-ray structure was done by forcing the torsion angles while all other parameters were optimized.

‡ 1 D = 3.33564 × 10⁻³⁰ C m.

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Structures of Two Spiro[cyclopropane-1,3'-indoline]-*cis,syn*-1,3-dimethyluracil Cyclobutane Photodimers

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Abstract. (1) 4a-(Spiro[cyclopropane-1,3'-indolin]-2'-yl)-1,3,6,8-tetramethyl-4a,4b,8a,8b-tetracyclobuta-[1,2-*d*:4,3-*d'*]dipyrimidine-2,4,5,7(1*H*,3*H*,6*H*,8*H*)-tet-

raone, C₂₂H₂₅N₅O₄, *M_r* = 423.52, monoclinic, *P*2₁/*c*, *a* = 7.868 (4), *b* = 14.167 (4), *c* = 18.340 (6) Å, β = 92.69 (4)°, *V* = 2042 (1) Å³, *Z* = 4, *D_m* = 1.37, *D_x* =

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