

Geometry of the Non-Planar Double Bond in *trans*-Cyclooctene. Structure of *trans*-2-Cycloocten-1-yl 3,5-Dinitrobenzoate

BY OTTO ERMER

Abteilung für Chemie, Ruhr-Universität, Universitätsstr. 150, D 463 Bochum, Federal Republic of Germany

AND SAX A. MASON

Institut Laue–Langevin, 156 X, F 38402 Grenoble CEDEX, France

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Abstract

The crystal structure of the title compound (I) has been studied at room temperature by X-ray and neutron diffraction. $C_{15}H_{16}N_2O_6$, m.p. 421 K, triclinic, space group $P\bar{1}$, $a = 10.963$ (2), $b = 5.656$ (1), $c = 14.873$ (2) Å, $\alpha = 104.91$ (1), $\beta = 122.75$ (1), $\gamma = 76.18$ (1)°, $U = 743.9$ Å³, $Z = 2$, $d_m = 1.41$, $d_c = 1.430$ g cm⁻³. $R = 0.052$ for 1623 observed X-ray reflections; 0.030 for 1824 observed neutron reflections. The *trans*-cyclooctene ring closely approximates C_2 symmetry. The non-planar deformation of the *trans* double bond is composed of 19.6 (3)° twisting and 22.3 (3)° (C_2 average) out-of-plane bending; the C=C=C-C torsion angle is 138.1 (1)° (neutron results). These values are in good agreement with electron-diffraction measurements and empirical force-field calculations for gaseous *trans*-cyclooctene.

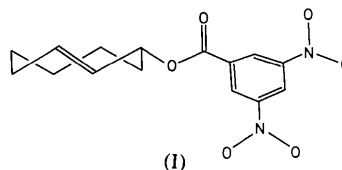
Introduction

trans-Cyclooctene is the smallest *trans*-cycloalkene stable at room temperature although obviously the pronounced non-planarity of its double bond leads to enhanced chemical reactivity. *trans*-Cycloheptene with a still more non-planar double bond is not stable at room temperature, although it exists at low temperature (Corey, Carey & Winter, 1965; Inoue, Ueoka, Kuroda & Hakushi, 1981). No observations have been reported so far which support the existence of *trans*-cyclohexene; however, according to computational evidence the existence of this highly strained olefin with an extremely non-planar double bond is not impossible (Ermer, 1981a).

Our interest in the double-bond geometry of *trans*-cyclooctene derives from empirical force-field calculations involving an olefin force field reported earlier (Ermer & Lifson, 1973). Such calculations represent an inductive computational scheme whose development

depends on close feed-back with experimental data, such as molecular energies, structures and vibrational frequencies, which serve to calibrate the force-field constants (Ermer, 1976, 1981a; Allinger, 1976). Of particular value in this respect is the experimental study of properties of highly strained molecules which allows us to examine and eventually extend the range of validity of the various potential energy terms of a force field. This range is limited due to the fact that the potential terms usually take very simple forms, e.g. harmonic approximations.

The non-planar double-bond deformations in *trans*-cyclooctene are among the largest known for olefins stable at room temperature. Their experimental study may thus be expected to furnish valuable information as to the performance of the potential terms in our force field which describe non-planar double-bond deformations. The structure of the free *trans*-cyclooctene molecule has been derived from gas electron-diffraction measurements (Trætteberg, 1975). Since *trans*-cyclooctene itself is not suitable for crystallographic structure analysis (m.p. 214 K), we have studied the crystal structure of a derivative, *trans*-2-cycloocten-1-yl 3,5-dinitrobenzoate (I), by means of X-ray methods, and briefly reported the experimental and force-field results (Ermer, 1974). Both structure analyses mentioned above yielded closely similar eight-ring geometries which are in good agreement with the results of our force-field calculations, as well as those of Anet & Yavari (1978), who used our non-planar double-bond deformation potentials. Structural force-field results for *trans*-cyclooctene of Allinger & Sprague (1972) agree less well with experiment.



Since the non-planar double-bond distortions do not in the present case consist simply of a twisting deformation, but also of out-of-plane bending, a more reliable determination of the H-atom positions at the *trans* double bond is desirable than is provided by electron and X-ray diffraction. Thus an accurate description of the double-bond geometry of *trans*-cyclooctene cannot be inferred from a knowledge of the carbon skeleton alone, but must also invoke reliable structural information about the H atoms concerned. We have therefore complemented our X-ray study by a neutron diffraction experiment, and the results of these crystal-structure analyses are described in the present paper.

Experimental

Triclinic crystals of (I) were grown by dissolving samples in acetone and subsequent slow replacement of the solvent by water in a desiccator. The cell constants and the X-ray intensities were measured at 295 K on a Hilger & Watts Y 290 four-circle diffractometer with Mo $K\alpha$ radiation (graphite monochromator). The X-ray intensities were converted to structure amplitudes without applying absorption corrections [$\mu(\text{Mo } K\alpha) = 1.3 \text{ cm}^{-1}$].

Neutron intensities were collected on the four-circle diffractometer D15 at the high-flux beam reactor of the Institut Laue-Langevin, Grenoble, using a crystal of approximate size $2.0 \times 1.5 \times 1.5 \text{ mm}$ [296 K; copper (331) monochromator; wavelength $1.1750(3) \text{ \AA}$, calibrated with $a = 6.2929 \text{ \AA}$ for a KCl standard crystal; $\omega/2\theta$ scan; measuring time per reflection *ca* 6 min]. The net reflection intensities were derived by the procedure of Lehmann & Larsen (1974). Absorption corrections were calculated by Gaussian integration assuming a linear absorption coefficient of 1.73 cm^{-1} , corresponding to an incoherent scattering cross-section of 40 barns for H (1 barn $\equiv 100 \text{ fm}^2$).

Structure solution and refinement

Positions for the 15 approximately coplanar heavy atoms of the dinitrobenzoate substituent of (I) were derived from a sharpened Patterson function, assuming space group $P1$. A subsequent difference Fourier synthesis with phases derived from these atomic positions yielded the C atoms of the eight-membered ring (Ermer, 1974). The X-ray least-squares refinement included anisotropic temperature factors for C, N and O and one common isotropic temperature factor for the H atoms (reflections with $\sin \theta/\lambda > 0.45 \text{ \AA}^{-1}$ were excluded in the hydrogen refinement). $\sum w(\Delta F)^2$ was minimized, with $w = 1/\sigma^2(F_o)$. Reflections with $F_o < 3\sigma(F_o)$ were excluded from the refinement. The X-ray scattering curves of Cromer & Waber (1965)

were used for the heavy atoms while that for (atomic) H was taken from *International Tables for X-ray Crystallography* (1968).*

The structural model fitted to the neutron diffraction data comprised anisotropic temperature factors for all

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36816 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Data for the structure analyses of *trans*-2-cycloocten-1-yl 3,5-dinitrobenzoate (I)

λ (Å)	X	0.71069 (Mo $K\alpha$)
	N	1.1750
$\sin \theta_{\text{max}}/\lambda$ (Å ⁻¹)	X	0.64
	N	0.58
$N_{\text{tot}}, N_{\text{ref}}$	X	2774, 1623
	N	2260, 1824
R, R_w	X	0.052, 0.045
	N	0.030, 0.025

N_{tot} is the total number of independent reflections measured, N_{ref} the number of reflections included in the refinements [$F_o \geq 3\sigma(F_o)$].

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^4$) with *e.s.d.*'s in parentheses

$U_{\text{eq}} = \frac{1}{3} \sum_{i=1}^3 U_{ii}$. The numbering of the atoms is given in Figs. 1 and 2(*d, f*). Common X-ray isotropic temperature factor for H = $0.024(2) \text{ \AA}^2$ (note that a scattering curve for atomic hydrogen was used which is responsible for this relatively small value).

		<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
C(1)	X	-1120 (3)	12423 (6)	3629 (2)	511 (20)
	N	-1119 (1)	12432 (3)	3631 (1)	442 (8)
C(2)	X	-866 (3)	9976 (6)	3468 (2)	478 (19)
	N	-869 (1)	9964 (3)	3466 (1)	401 (7)
C(3)	X	-1093 (3)	8693 (5)	2399 (2)	478 (18)
	N	-1086 (1)	8677 (2)	2399 (1)	398 (7)
C(4)	X	-2692 (3)	8237 (5)	1686 (2)	544 (20)
	N	-2698 (2)	8227 (3)	1679 (1)	462 (8)
C(5)	X	-3781 (3)	10586 (6)	1642 (2)	524 (19)
	N	-3779 (2)	10563 (3)	1640 (1)	451 (9)
C(6)	X	-4057 (3)	11457 (6)	2605 (3)	590 (21)
	N	-4063 (2)	11438 (3)	2601 (1)	510 (9)
C(7)	X	-3528 (3)	13878 (6)	3349 (2)	581 (21)
	N	-3531 (2)	13883 (3)	3351 (1)	480 (8)
C(8)	X	-1889 (3)	13735 (6)	4218 (3)	595 (21)
	N	-1890 (2)	13740 (3)	4220 (1)	503 (9)
C(9)	X	1211 (3)	2926 (5)	2048 (2)	447 (18)
	N	1205 (1)	2921 (2)	2049 (1)	370 (7)
C(10)	X	1509 (3)	1474 (5)	1262 (2)	438 (17)
	N	1503 (1)	1478 (2)	1259 (1)	369 (7)
C(11)	X	2386 (3)	-733 (5)	1485 (2)	450 (18)
	N	2387 (1)	-746 (2)	1482 (1)	369 (7)
C(12)	X	2983 (3)	-1574 (5)	2451 (2)	475 (18)
	N	2988 (1)	-1605 (2)	2449 (1)	401 (7)
C(13)	X	2682 (3)	-81 (5)	3209 (2)	459 (18)
	N	2682 (1)	-90 (2)	3215 (1)	396 (7)
C(14)	X	1811 (3)	2149 (5)	3036 (2)	473 (18)
	N	1810 (1)	2155 (2)	3040 (1)	391 (7)
C(15)	X	227 (3)	5312 (5)	1791 (2)	495 (19)
	N	221 (1)	5304 (2)	1793 (1)	403 (7)

Table 2 (cont.)

		x	y	z	U_{eq}
N(1)	X	2713 (3)	-2307 (5)	658 (2)	586 (18)
	N	2711 (1)	-2302 (2)	659 (1)	496 (6)
N(2)	X	3292 (3)	-921 (5)	4251 (2)	639 (18)
	N	3292 (1)	-940 (2)	4248 (1)	533 (6)
O(1)	X	-142 (2)	6307 (3)	2538 (2)	595 (13)
	N	-144 (2)	6312 (3)	2537 (1)	498 (9)
O(2)	X	-161 (2)	6184 (4)	1013 (2)	722 (15)
	N	-163 (2)	6183 (3)	1015 (1)	611 (10)
O(3)	X	2145 (3)	-1608 (4)	-205 (2)	790 (17)
	N	2148 (2)	-1616 (4)	-201 (2)	683 (12)
O(4)	X	3523 (3)	-4201 (5)	892 (2)	919 (20)
	N	3520 (3)	-4194 (4)	889 (2)	833 (15)
O(5)	X	3745 (3)	-3096 (5)	4295 (2)	969 (20)
	N	3744 (3)	-3110 (4)	4291 (2)	853 (15)
O(6)	X	3301 (3)	570 (5)	4996 (2)	921 (20)
	N	3300 (3)	560 (4)	4993 (2)	811 (14)
H(1)	X	-1089 (24)	13289 (41)	3131 (17)	
	N	-1092 (4)	13442 (6)	3124 (3)	813 (23)
H(2)	X	-960 (25)	8943 (41)	3870 (18)	
	N	-939 (4)	8916 (6)	3942 (3)	705 (19)
H(3)	X	-832 (24)	9634 (41)	2051 (18)	
	N	-828 (3)	9742 (6)	2022 (3)	672 (18)
H(41)	X	-2906 (25)	7577 (42)	961 (18)	
	N	-2920 (4)	7462 (7)	855 (3)	765 (23)
H(42)	X	-2856 (25)	6939 (41)	1972 (18)	
	N	-2869 (4)	6833 (7)	1976 (3)	818 (23)
H(51)	X	-4687 (24)	10247 (41)	1016 (18)	
	N	-4819 (4)	10186 (8)	904 (3)	788 (24)
H(52)	X	-3439 (24)	12053 (40)	1555 (17)	
	N	-3468 (4)	12086 (7)	1504 (3)	779 (22)
H(61)	X	-5114 (24)	11711 (41)	2298 (17)	
	N	-5245 (4)	11702 (8)	2247 (3)	914 (27)
H(62)	X	-3713 (25)	10038 (41)	3020 (18)	
	N	-3637 (4)	9978 (7)	3086 (3)	881 (24)
H(71)	X	-4079 (24)	14490 (41)	3715 (18)	
	N	-4128 (4)	14552 (7)	3773 (3)	839 (23)
H(72)	X	-3760 (25)	15134 (41)	2871 (18)	
	N	-3800 (4)	15245 (6)	2863 (3)	745 (22)
H(81)	X	-1621 (24)	15451 (42)	4539 (17)	
	N	-1602 (4)	15588 (7)	4617 (3)	813 (24)
H(82)	X	-1780 (24)	12696 (41)	4714 (17)	
	N	-1667 (4)	12707 (8)	4822 (3)	793 (23)
H(10)	X	1111 (24)	2017 (41)	598 (18)	
	N	1056 (3)	2103 (5)	493 (2)	583 (17)
H(12)	X	3570 (24)	-3165 (40)	2562 (17)	
	N	3670 (3)	-3352 (6)	2605 (2)	641 (18)
H(14)	X	1667 (24)	3104 (40)	3574 (18)	
	N	1605 (3)	3280 (5)	3668 (2)	639 (17)

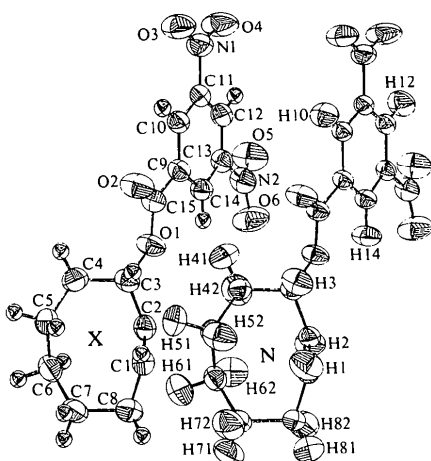


Fig. 1. The structure of (I), showing the atomic numbering. Thermal ellipsoids are at the 50% probability level (X: X-ray; N: neutron).

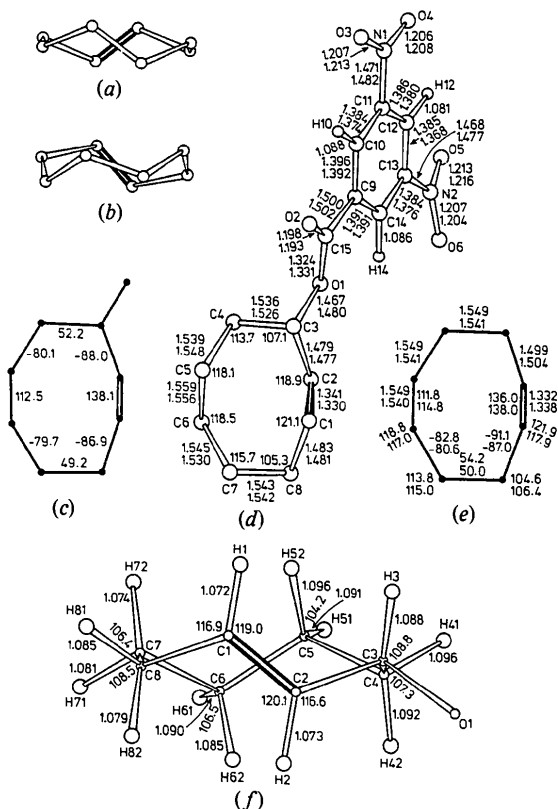


Fig. 2. (a) Crown and (b) distorted chair conformation of *trans*-cyclooctene. (c) Neutron torsion angles in the eight-membered ring ($^{\circ}$); average e.s.d. 0.2° . (d) Neutron (upper) and X-ray (lower) bond lengths, neutron aromatic CH bond lengths (\AA); average e.s.d.: CC, CO, CN, NO 0.002 (N), 0.004 (X); CH 0.004 \AA ; and neutron CCC angles in the eight-membered ring ($^{\circ}$); average e.s.d. 0.1° . (e) Bond lengths (\AA), bond angles and torsion angles ($^{\circ}$) for *trans*-cyclooctene; upper, gas electron-diffraction measurements (Trættestad, 1975); lower, force-field calculations (Ermer, 1974). (f) Neutron bond lengths (\AA) and angles ($^{\circ}$) involving H atoms in the *trans*-cyclooctene system; average e.s.d. CH 0.004 \AA , HCC 0.2 , HCH 0.3° .

atoms. The nuclear scattering lengths applied were taken from the compilation of Bacon (1962). Reflections with $F_o < 3\sigma(F_o)$ were again excluded from the refinement. F_o/F_c comparisons did not indicate substantial extinction effects for either X-ray or neutron diffraction data; thus no corrections were considered.* Table 1 summarizes further details of the structure analyses.

The refined atomic coordinates from the X-ray and neutron diffraction measurements are given in Table 2. The labelling of the atoms is shown in Figs. 1 and 2(d,f). Fig. 1 illustrates the atomic thermal ellipsoids. Figs. 2 and 3 show X-ray and neutron bond lengths, and neutron bond angles and torsion angles.

* See deposition footnote.

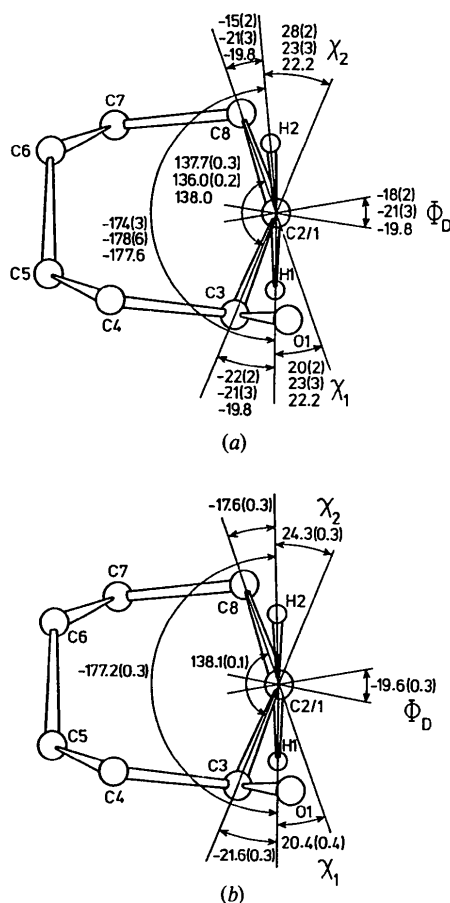


Fig. 3. Newman projections along the double bond showing the non-planar deformation parameters of the *trans*-cyclooctene double bond ($^{\circ}$) with e.s.d.'s in parentheses (dinitrobenzoyl substituent omitted). (a) Upper, present X-ray analysis for (I); middle and lower, gas electron diffraction (Trætterberg, 1975) and force-field calculation (Ermer, 1974) for *trans*-cyclooctene. (b) Present neutron diffraction measurement for (I).

Discussion

The eight-membered ring possesses the crown conformation which is characterized by alternating signs of the CCCC torsion angles (Fig. 2a). The C_2 symmetry which results for this conformation from the force-field calculations and which was assumed in the gas electron-diffraction analysis of Trætterberg (1975) is closely approximated in crystalline (I); cf. the torsion angles in Fig. 2(c). The data of a somewhat earlier electron-diffraction measurement of *trans*-cyclooctene by Gavin & Wang (1973) were interpreted in terms of a C_2 -symmetric distorted chair conformation (Fig. 2b) which according to our calculations is energetically less favorable than the crown (Ermer, 1974). These discrepancies, which apparently have their origin in shortcomings of Gavin & Wang's (1973) study, are discussed elsewhere (Ermer, 1974, 1976, 1981a).

Further results of detailed conformational analytical calculations for *trans*-cyclooctene, concerning in particular its racemization and *trans/cis*-isomerization mechanisms, have been presented recently (Ermer, 1981a).

Out-of-plane (o.o.p.) deformations of an olefinic double bond may be analyzed in terms of three different basic types: pure twisting, symmetric o.o.p.-bending, and antisymmetric o.o.p.-bending (Fig. 4a-c) (Herzberg, 1945). Symmetry conditions may be formulated for the three basic types of o.o.p.-deformations as well as for their combinations (Ermer, 1981a). The symmetry condition for a combined twisting and symmetric o.o.p.-bending deformation (Fig. 4d) is a single twofold axis through the center of the double bond and perpendicular to the best plane through the six atoms defining the double bond. This condition is met by suitable *trans* double bonds as in the C_2 -symmetric crown conformation of *trans*-cyclooctene. The symmetry condition for a combination of twisting and antisymmetric o.o.p.-bending (Fig. 4e) is a single twofold axis perpendicular to the double bond and lying in the best plane through the six double-bond atoms. This type of deformation occurs in suitable non-planar *cis* double bonds; e.g. in twistene (tricyclo[4.4.0.0^{3,8}]-dec-4-ene; Ermer, 1981a) or in crystalline phthalic acid (Ermer, 1981b).

Two different ways of superimposing twisting and symmetric o.o.p.-bending deformations are conceivable in the C_2 -symmetric crown conformation of *trans*-cyclooctene (Fig. 5a and c). The arrangement of Fig. 5(a) with the double-bond H atoms bent inward towards the center of the eight-membered ring is energetically more favorable since this type of deformation leads to a reduction of double-bond twisting. This had earlier been predicted on thermochemical grounds by Dunitz (1968) for the analogous, yet less extreme case of *trans*-cyclodecene.

As geometrical double-bond twisting parameter ϕ_D we use for *trans*-cyclooctene the arithmetic mean of the two C=C-H torsion angles. The o.o.p.-bending deformations are described as linear combinations of the so-called χ parameters assigned to each sp^2 C atom,

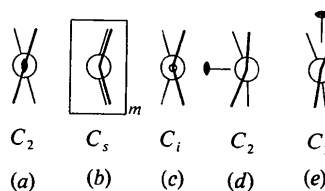


Fig. 4. Possible non-planar double-bond deformations (schematic Newman projections along double bond). (a) Twisting, (b) symmetric out-of-plane (o.o.p.) bending, (c) antisymmetric o.o.p.-bending, (d) combination of twisting and symmetric o.o.p.-bending, (e) combination of twisting and antisymmetric o.o.p.-bending. The symmetries required for the various deformation possibilities are given (Ermer, 1981a).

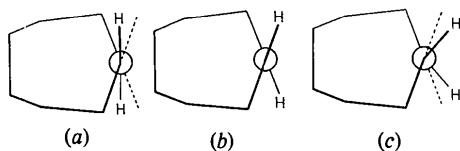


Fig. 5. Non-planar double-bond deformations in the C_2 -symmetric crown conformation of *trans*-cyclooctene. (a) Energetically favorable combination of twisting and symmetric o.o.p.-bending, (b) pure twisting, (c) unfavorable combination of twisting and symmetric o.o.p.-bending. The non-planar double-bond deformation energy increases from (a) to (c).

i.e. to C(1) and C(2). χ_1 is defined as the deviation from 180° of the angle between the planes through H(1), C(1), C(2) and C(8), C(1), C(2); χ_2 represents the deviation from 180° of the H(2), C(2), C(1)/C(3), C(2), C(1) dihedral angle (see Fig. 3). χ_1 and χ_2 may be evaluated from the 'improper' torsion angles, H(1)···C(2)=C(1)—C(8) and H(2)···C(1)=C(2)—C(3) (Warshel, Levitt & Lifson, 1970; Ermer, 1981a).

The experimental values for the twist angle φ_D and the o.o.p.-bending angles χ_1 and χ_2 of the *trans*-cyclooctene double bond in (I) are -18 (2), 20 (2) and 28 (2) $^\circ$ from the X-ray study (Fig. 3a), and -19.6 (3), 20.4 (4) and 24.3 (3) $^\circ$ from the neutron diffraction measurement (Fig. 3b). The neutron results for these parameters are thus about seven times more precise than the X-ray values. χ_1 and χ_2 would be equal had the *trans* double bond exact C_2 symmetry. The observed difference Δ_x of 3.9 (5) $^\circ$ (neutron diffraction) may be ascribed to substituent and/or packing effects. The X-ray and neutron diffraction values for the C—C=C—C torsion angle are 137.7 (3) and 138.1 (1) $^\circ$. The large deviation of 41.9° from planarity is thus composed of 19.6° twisting and $\frac{1}{2}(24.3 + 20.4) = 22.35^\circ$ o.o.p.-bending (neutron values; Fig. 3b).

The twisting and C_2 -averaged χ parameters resulting from the neutron diffraction study are in almost perfect agreement with the values calculated from our olefin force field: $\varphi_D = -19.8$, $\chi_1 = \chi_2 = 22.2^\circ$ (Fig. 3a,b) (Ermer, 1974). The calculated C—C=C—C torsion angle of 138.0° therefore also agrees well with the experimental values. The double-bond twisting and o.o.p.-bending potential functions of our force field are essentially quadratic for deformations of the magnitude present in *trans*-cyclooctene. The respective potential constants were largely derived from the o.o.p.-vibrational frequencies of ethylene and a number of other olefins, and to a lesser extent by considering an experimental value for the *trans*-cyclooctene C—C=C—C torsion angle taken from a rough X-ray analysis of a *trans*-cyclooctene heavy-atom derivative (Ferguson & Hawley, 1971; Ermer & Lifson, 1973). The good agreement in particular of the reliable neutron double-bond geometry in (I) with the calcu-

lated results for gaseous *trans*-cyclooctene allows the conclusion that the potential terms for double-bond twisting and o.o.p.-bending in our force field satisfactorily describe the related deformations up to values of at least 20° . Obviously, this conclusion neglects substituent and packing effects; however, the good agreement of Trætteberg's (1975) electron-diffraction results with those of both the neutron diffraction experiment and the force-field calculation suggests that the perturbation of the *trans* double-bond geometry in (I) by such effects is rather small.

The correctly calculated twisting and o.o.p.-bending contributions to the non-planarity of the double bond in *trans*-cyclooctene represented a true prediction since no experimental o.o.p.-bending angles were available at the time of the development of our force field. This prediction was thus essentially based on the assumption that the spectroscopic o.o.p.-deformation potentials for olefinic double bonds are transferable to structural calculations.

As expected, the neutron length of 1.341 (2) Å (Fig. 2d) for the non-planar double bond in (I) is somewhat larger than in normal olefins with planar double bonds [$r_\alpha^o(\text{C}=\text{C}) = 1.334$ (4) Å in propene; gas electron-diffraction study (Tokue, Fukuyama & Kuchitsu, 1973; r_α^o is a positional vibrational average and therefore an appropriate distance parameter for comparison with a crystal-structure analysis)]. The X-ray value for this bond length is 0.011 Å smaller (Fig. 2d) and this is probably due to the relatively high electron density in the double bond which tends to move the double-bond C atoms somewhat closer together in the X-ray refinement. In tetracyanoethylene the C=C bond length determined by neutron diffraction is also 0.011 Å longer than the corresponding distance obtained from X-ray data (Becker, Coppens & Ross, 1973).

According to simple hybridization considerations one might expect that in *trans*-cyclooctene the double-bond electron density outside the eight-membered ring is higher than inside. The X-N difference electron densities in three sections through the double bond in (I) are shown in Fig. 6. However, since the difference maps are based on room-temperature data, some caution should be exercised in drawing conclusions from them (*cf.* Scheringer, Kutoglu & Mullen, 1978). Nonetheless, it is of interest to note that there are apparently no significant deformation-density differences between the two sides of the double bond.

As is usually found in similar studies, the atomic vibrational mean square amplitudes derived from the neutron data are systematically smaller than those resulting from the X-ray refinement (Table 2, Fig. 1). The average differences ΔU_{11} , ΔU_{22} , and ΔU_{33} amount to 12, 18, and 15% of the X-ray values. These differences are due to the influence of the aspherical electron-density distributions in the chemical bonds and

Table 3. Results of the rigid-body-motion calculations

Molecular fragment		R.m.s. (ΔU) (\AA^2)	R.m.s. [$\sigma(U)$] (\AA^2)	Eigenvalues of L (deg 2)	Eigenvalues of T ($\text{\AA}^2 \times 10^3$)	Librational bond-length corrections (\AA)
C(1)–C(8)	X	0.0020	0.0018	38, 18, 7	54, 44, 35	0.007–0.012
	N	0.0011	0.0008	48, 17, 8	45, 34, 26	0.006–0.014
C(9)–C(15), N(1), N(2)	X	0.0017	0.0017	19, 7, 4	49, 45, 37	0.002–0.005
	N	0.0010	0.0006	16, 6, 4	44, 35, 28	0.002–0.005

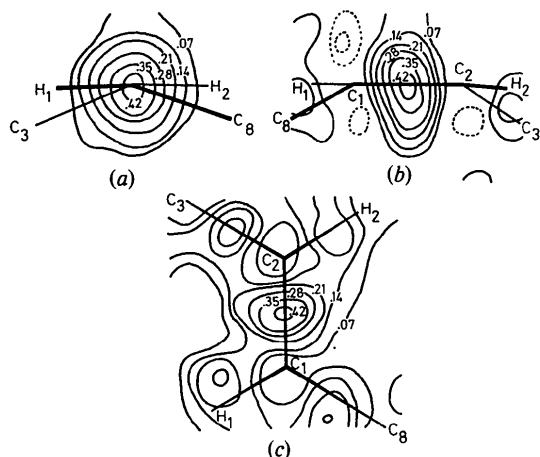


Fig. 6. X–N difference-density sections through the *trans* double bond of (I). (a) Section perpendicular to the double bond through its mid-point, (b) section perpendicular to the best plane through the six atoms defining the double bond, (c) section in this plane. Contour interval 0.07 e \AA^{-3} ; e.s.d. $\text{ca } 0.1 \text{ e \AA}^{-3}$.

lone pairs which tends to inflate somewhat the thermal-motion parameters in the X-ray refinement (Coppens, 1975).

An attempt was made to interpret the anisotropic temperature factors in terms of rigid-body motion (Schomaker & Trueblood, 1968). It was found that such a model provides a reasonable description of the observed thermal motion of the two molecular fragments comprising the C atoms of the eight-membered ring and the atoms C(9)–C(15), N(1), N(2), respectively. Larger molecular fragments involving O and H atoms give poor rigid-body fits. Details of the rigid-body calculations are summarized in Table 3. The larger X-ray thermal-motion parameters express themselves primarily in an increased translational rigid-body motion as compared to the neutron data. The librational amplitudes for both fragments differ considerably suggesting substantial relative librational (or rather vibrational torsional) motion between them. The translational amplitudes of both fragments are similar indicating their validity for the molecule as a whole; this result is not surprising and is supported by an analysis of the respective eigenvectors.

The X-ray and neutron lengths of the double bond corrected for libration are 1.337 and 1.350 \AA , respec-

tively. The librational corrections for the non-planar deformation parameters of this bond are negligible. The (neutron) C–H bond lengths suffer from considerably larger shortening effects than the heavy-atom bond lengths (up to 0.04 \AA ; Fig. 2*d,f*). This is due to the combined influence of libration and internal vibrations which both lead to large motion of the H atoms, the former because of their peripheral positions and the latter because of their small mass.

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Structure of a 1:1 Molecular Complex of 9-Methyladenine and 2-Thiohydantoin

BY ROBERT E. CASSADY* AND STUART W. HAWKINSON

Department of Biochemistry, University of Tennessee, Knoxville, Tennessee 37916, USA

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Abstract

The 1:1 molecular complex of 9-methyladenine and 2-thiohydantoin ($C_6H_7N_5 \cdot C_3H_4N_2OS$) is monoclinic, space group $C2/c$ with unit-cell parameters $a = 21.140$ (3), $b = 7.085$ (1), $c = 16.101$ Å and $\beta = 103.27$ (2)°, with eight complexes per unit cell ($D_c = 1.499$, $D_o = 1.508$ Mg m⁻³). The intensity data were collected on an automated diffractometer using Nb-filtered Mo $K\alpha$ radiation, and the structure was solved using direct methods. The structure was refined in two blocks (non-hydrogen atoms anisotropic, hydrogens isotropic); the refinement converged to a final conventional $R(f)$ value of 3.5% (4.9% weighted) for the 2475 significant data. The structure consists of ribbons with alternating adenine and hydantoin moieties linked *via* (hydantoin)N—H...N(adenine) hydrogen bonds. The ribbons are held together *via* N—H...N hydrogen bonds involving the 9-methyladenine molecules. The sulfur and oxygen atoms of the 2-thiohydantoin molecules do not appear to act as acceptors in strong hydrogen bonds.

Introduction

There is considerable interest in the hydrogen-bonding characteristics in complexes of adenine derivatives with substituted hydantoins (Jones & Kemp, 1974) and

barbiturates (Hsu & Craven, 1974; Shieh & Voet, 1976*a,b*). This laboratory is currently investigating complexes of 9-methyladenine and various substituted hydantoins in an effort to characterize further these interactions. We were particularly interested in the role sulfur might play in hydrogen bonding.

Experimental

Crystals of the 1:1 complex of 9-methyladenine and 2-thiohydantoin were obtained in the form of yellow rectangular plates from hot water containing equimolar quantities of 9-methyladenine (Cyclo Chemical) and 2-thiohydantoin (Sigma Chemical). A crystal of the complex with dimensions 0.21 × 0.15 × 0.08 mm was chosen for diffraction study. The crystal density (1.508 Mg m⁻³), which was determined by flotation in a mixture of cyclohexane and dibromoethane, agrees with the calculated value (1.499 Mg m⁻³), assuming eight molecules of each component in the unit cell. The space group and approximate cell dimensions were obtained from precession and Weissenberg photographs. Accurate cell dimensions (*Abstract*) were obtained by the least-squares refinement of the observed setting angles for fourteen Mo $K\alpha$ reflections in the range $28 < 2\theta < 44^\circ$, measured with an Oak Ridge computer-controlled diffractometer (Busing, Ellison, Levy, King & Rosenberry, 1968). Intensity data were collected on the diffractometer with Nb-filtered Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) using the θ - 2θ scan technique. Of the 2710 reflections with $2\theta \leq 55^\circ$, 2475

* To whom correspondence should be addressed. Present address: Department of Chemistry, Medical Center Hospital, 400 State of Franklin Road, Johnson City, Tennessee 37601, USA.