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A Statistical Approach to the Geometry of Norbornane from X-ray Data of Substituted Derivatives

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Abstract

From the Cambridge Crystallographic Data File the structures of norbornane derivatives were collected and the distributions of internal parameters (bond lengths, valence angles and torsion angles) analysed for the norbornane fragments. Comparison of the median values of these distributions with the gas-phase structure of free norbornane yields an excellent correspondence for angles but not for bond distances. The variance of the distributions of the different parameters is related to the force constant of the same parameter in free norbornane.

Introduction

Recently the gas-phase structure of norbornane§ (Fig. 1) has been determined by electron diffraction (GED), combined with microwave, infrared and Raman spectroscopic data (Doms, Van den Enden, Geise & Van Alsenoy, 1983). This analysis yielded very precise values for the mean CC bond and certain valence angles, but the lengths of the individual CC bonds [C(1)–C(2), C(2)–C(3) and C(1)–C(7)] remained largely unresolved. Fig. 2 shows a contour plot of the disagreement factor R of the GED least-squares analysis as a function of the differences between bond lengths [$\Delta_1 = $ C(1)–C(7) $-$ C(1)–C(2) and $\Delta_2 = $ C(2)–C(3) $-$ C(1)–C(2)]. The inner contour encloses all solutions which are acceptable at the 95% significance level; the outer contour encloses the solutions which are still acceptable at the 99·5% signifi-

cance level. It is clear that the accuracy of the individual CC bond distances is only of the order of 0·02–0·03 Å and that the sequence of the C(1)–C(7) and C(1)–C(2) bond distances cannot be determined. Also, the order of some valence angles remained uncertain. Since in the analysis all available structural data of gaseous norbornane had been exhausted, any additional information has to come from another phase. Here we question the possibilities, if any, of reducing the remaining uncertainties by taking into account information that is available from single-crystal X-ray determinations.

Difficulties of preparing suitable single crystals have so far prevented the X-ray determination of norbornane, but many structures of substituted norbornane derivatives are known.

Statistical studies on large sets of substituted compounds have produced useful structural details for cyclopropane (Allen, 1980, 1981a), benzene (Allen, 1981b; Domenicano, Vaciago & Coulson, 1975a, b), hetero-atomic rings (Norrestam & Schepper, 1981) and *tert*-butoxy groups (De Vos, Schreurs, Kroon & Van Duijneveldt, 1983). The purpose of these studies was to evaluate the influence of substituents on the geometry of the common fragment. To this end the molecules in the sample were grouped as a function of mutual disposition and electronic properties of the substituents.

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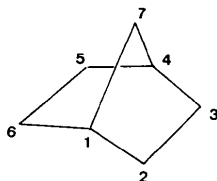
§ The IUPAC name is 8,9,10-trinorbornane.

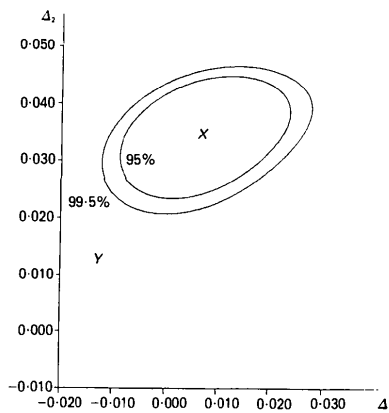Fig. 1. The structural formula of norbornane with numbering of atoms.

Fig. 2. Contour plot of R values as function of Δ_1 and Δ_2. X denotes the best-fitting model of the electron diffraction analysis, Y a model based on the averaged X-ray fragments.

Table 1. *Bibliography*

Each X-ray structure in the CCDF is identified by the CCDF reference code (Allen *et al.*, 1979). It consists of six alphabetic characters identifying the compound and a possible two digits which trace the publication history. Compounds used in the analysis are listed below by their reference codes. Since none of the individual structures is explicitly referrred to, we have omitted all further details. Compound names can be retrieved from the CCDF using the reference codes. Full literature citations have been deposited.

AMTTCD*	AMTTCD*	BIFENY†	BIFENY†	BMCLMH†
BMPDOD	BPICAM	BPICAM	BRTCNO	BSCHCX10
BTCNDE	BTCUNO10	BXHPCD	BXHPCD	(BXNBRT10)‡
BXNBRT10	(BXNBRT10)	BZEHPN†	BZEHPN†	CALBPD10
CAMCBX10†	CAMCBX10†	CAMPHX10†	CAMPHX10†	CAMQNI
CAMQNI†	CETDEO10	CHASIN	CHGALD§	(CHGALD)
(CHGCAM)	CSPHTD	CSPHTD	CXBEFH†	DCTCTO
DCTCTO	DHXCAM†	DHXCAM†	DNBOIM	DTIBOX
EAATPB10	EBTCON§	ENBZAM	EPMVZN	EXCPNB
(FSTCTD)	FSTCTD*	HAMCHC	HCYTAG*	(HCYTAG)
HCYTAG*	HFPCTD10	HMCYDL10§	HMEMHN	HMHPCX
(HMNCXA)	HMNCXA*	HMNCXB	HMNCXB	HMNCXC
HMNCXC	HPCCAM	(HTCTDD)	(HTCTDD)	(HTCTDD)
(HTCTDD)	IPCUND*	IPCUND*	IPCUND*	MBLVBT
MBMCYD10	MCNFCH10	MENPHL*	(MENPHL)	MEXOFE†
MEXOFE†	MHBCHP†	MHBHPC	MPHHCM	MPHHCM
MXDSAD	MXNBFE†	NCAMCU*	NCAMCU*	OCMUNO§
OCTHEN	OCTHEN	PCCHLD	PCCHLD	PSCOPS20
PTCHLD*	PTCHLD*	PTCHLD*	PTCHLD*	PTCHLD*
SOLAOX	TCAMNO	THHCOD10	THHCOD10	VINDCP10
(XBXMHPI0)				

* Omitted because of fusion with equally or more strained ring system.

† Omitted because of the presence of sp^2-hybridized C atoms.

‡ Entries in parentheses omitted because either $R > 0.10$ or e.s.d. (C–C) > 0.03 Å.

§ Omitted because of the presence of a single-atom bridge.

The great diversity of substituents encountered prevents such an approach in the case of norbornane. Moreover, in contrast to the above studies, we hope that it is possible to deduce relevant gas-phase values of the parent hydrocarbon from distributions in a sample of subsituted derivatives in the solid state.

In other words, we hope that $x_g \simeq x_o \simeq \langle x \rangle$, where x_g is the gas-phase value, x_o the solid-phase value of a parameter x in the parent hydrocarbon and $\langle x \rangle$ the average value of $P(x)$, the distribution of x in the substituted derivatives. The assumption $x_g \simeq x_o$ is justified by the observation that it holds reasonably well for cyclopropane and benzene, while $x_g \simeq \langle x \rangle$ finds justification in the fact that the average CC bond length observed in unsubstituted norbornane in the gas phase (1·547 Å) is very close to the value (1·546 Å) obtained after averaging over our complete sample space. The second purpose of this work concerns the information provided by $P(x)$. If the influence of substituents (Van Hemelrijk, Lenstra & Geise, 1982) and measuring errors is small (r.m.s. values ranging from 0·003 Å to 0·03 Å for CC bonds) compared to variations due to thermal motion (r.m.s. values *ca* 0·05 Å for CC bonds), then $P(x)$ will resemble a distribution of 'snap-shots' of the free molecule. The latter is normally distributed (Cyvin, 1968) provided anharmonicity effects can be ignored. Therefore, we will examine for each parameter whether the sample distribution is normal, and, if so,

compare its spread with the r.m.s. vibrational amplitude of the free molecule.

It seems appropriate to discuss at this point the parameter type we wish to compare. A gas-phase electron diffraction analysis usually results in a set of internal parameters of the r_g type. Each parameter represents the average of a distribution caused by thermal vibrations. A principally different set, the r_α type, obtains when one calculates distances and angles from averaged Cartesian coordinates. It follows that r_α parameters rigorously preserve geometric consistency, whereas r_g parameters may not. The difference between r_g and r_α parameters is small; it is of the order of a few thousandths of an Å for bond lengths and a few tenths of a degree for valence angles (Kuchitsu & Cyvin, 1972).

Each individual parameter in our sample of crystal structures was calculated from atomic coordinates and would thus resemble an r_α parameter. Therefore, we will compare the solid-state results with electron diffraction values of norbornane in the gas phase converted to r_α type.

Finally it should be noted that the averages (or median values) of distributions of X-ray parameters no longer constitute a geometrically consistent set. In our case the inconsistency, less than 0·5° in valence angles, may be ignored.

Data retrieval and data set

With the Cambridge data retrieval package (Allen *et al.*, 1979) the Cambridge Crystallographic Data File (CCDF) was searched for all molecular structures published in the period 1976–1980 containing the norbornane skeleton (see Table 1). From the 101 structures in the list we omitted 12 entries with an R value larger than 0·10, one entry with σ(C–C) > 0·03 Å and 17 entries in which the norbornane skeleton contained C(sp^2)-hybridized atoms. From the remaining sample we further discarded structures in which the norbornane fragment is also part of another structural fragment which is equally or more severely strained than norbornane itself. The last criterion is needed because of the existence of what may be called 'pell-mell' structures: compounds containing two or more norbornane skeletons sharing a CC bond, which belongs to a different distance type in each norbornane fragment. Fig. 3 shows an example of a pell-mell structure. In these cases the distinction between the three types of CC bonds is lost. In the limit of an infinite sample of pell-mell structures all mean CC distances become equal and consequently these compounds cannot give information relevant to free norbornane. Furthermore, if one of the CC bonded distances of the norbornane skeleton is part of another strained structure we assume that its length is more indicative of the most severely strained fragment. The concept 'more' or

Table 2. *Some characteristics of the distributions of bond lengths* (Å) *and valence angles* (°)

	C(1)-C(2)	C(2)-C(3)	C(1)-C(7)	C(2)-C(1)-C(7)	C(2)-C(1)-C(6)	C(1)-C(2)-C(3)	C(1)-C(7)-C(4)
Number of entries	204	102	102	204	102	204	51
Minimum value	1·485	1·485	1·505	82·7	95·6	96·5	90·8
Maximum value	1·635	1·618	1·618	109·5	119·4	106·2	96·7
Mean	1·5462	1·5589	1·5388	101·7	107·1	102·6	94·2
Median	1·5435	1·5585	1·5345	101·8	108·2	103·0	94·3
Variance	0·00055 Å^2	0·00048 Å^2	0·00038 Å^2	6·5	20·8	2·5	1·3
Normally distributed	Yes	Yes	No	Yes	No	No	Yes

'less' strained is thus defined here in terms of the deformability of the norbornane fragment compared to the other fragment. As a measure of deformability we take the lowest vibrational frequency of the molecule consisting of the fragment under consideration filled up with H atoms. If this frequency is higher than the lowest vibrational frequency of norbornane, then the fragment is considered the more strained and the entry is omitted from the data set.

When the necessary spectroscopic data were lacking, elements of the set were discarded if (*a*) one single atom of a substituent connects two adjacent atoms of the norbornane skeleton and (*b*) the substituent is polycyclic, contains a zero- or one-atom bridge and shares a bond with the norbornane skeleton.

After having applied all these criteria to the sample 51 structures remained. Their structural parameters were combined in 11 different samples corresponding to the three different CC bond lengths, the four different CCC valence angles and the four torsion angles (Fig. 4). By this choice we impose C_{2v} symmetry on the average norbornane structure.

Analysis of the data*

Bond lengths

The distributions of bond lengths (Fig. 4) were tested for the hypothesis H_o: the distribution is normal. The tests were executed at the 97·5% significance level using contingency tables and the χ^2 test. Some characteristics are given in Table 2. The hypothesis

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* Full references and contingency tables corresponding to Fig. 4 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP42154 (15pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
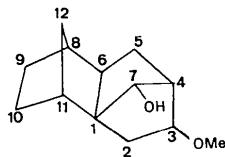
Fig. 3. Example of a pell-mell structure. Note that C(1)C(2)C(3)C(4)C(5)C(6)C(7) constitute one norbornane fragment and C(1)C(6)C(8)C(9)C(10)C(11)C(12) another. Ambiguities arise because, *e.g.*, C(1)-C(6) is an r_{12}-type distance in the first and an r_{23}-type distance in the second norbornane skeleton.
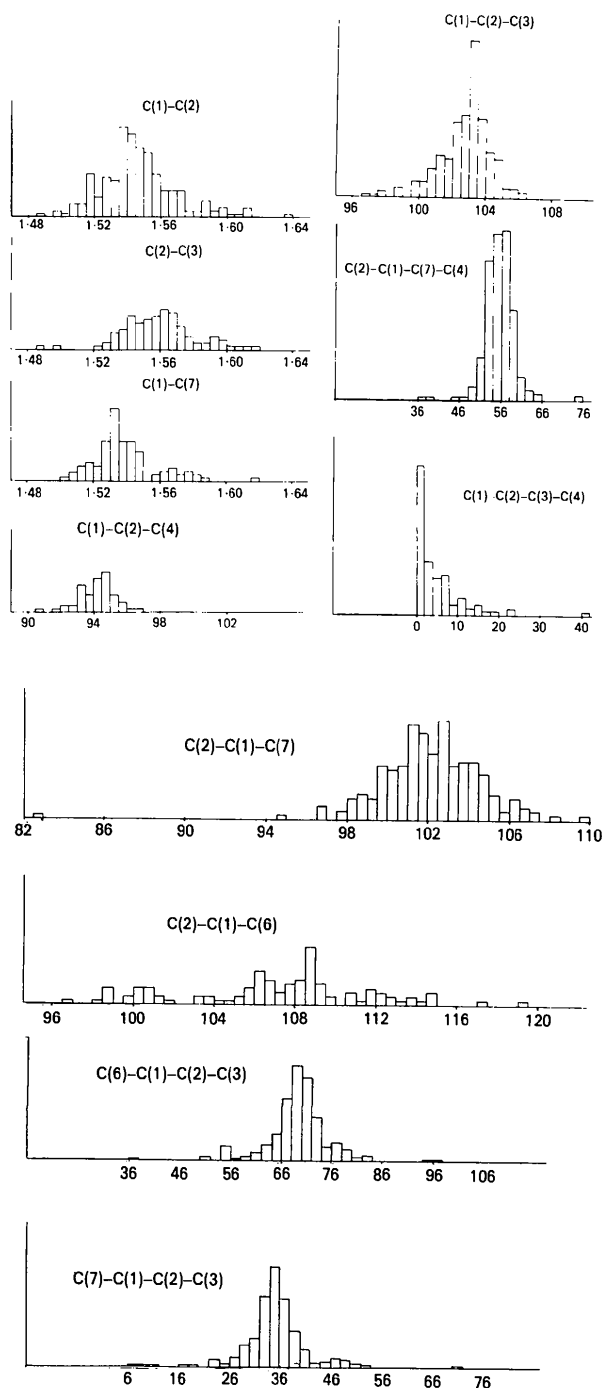
Fig. 4. Histograms of the various internal coordinates.

Table 3. *Comparison of the standard deviation of each sample distribution with vibrational parameter of free norbornane*

	S_i (Å)	U_i^* (Å)	k_i†	U_i/S_i
C(1)-C(2)	0·0234	0·0592	3·34	2·530
C(2)-C(3)	0·0218	0·0551	3·64	2·528
C(1)-C(7)	0·0194	0·0523	4·33	2·696
C(1)-C(2)-C(3)	1·59°		0·84	
C(6)-C(1)-C(2)	4·56		1·86	
C(2)-C(1)-C(7)	2·56		0·71	
C(1)-C(7)-C(4)	1·14		1·14	

* Vibrational amplitude determined in GED experiment.
† Force constant ($\times 10^{-8}$ N Å^{-1} for bond distances, $\times 10^{-8}$ N for angles) determined from vibrational frequencies of norbornane in the gaseous and the solid phase.

H_o could not be rejected for the samples corresponding to C(1)-C(2) and C(2)-C(3). We then treat the values of mean and median as equal. Next we tested whether the standard deviation S_i of the distribution is coupled to the deformability of the bond at hand, measured by the stretching-force constant or more directly by the amplitude of vibration U_i of the bonded distance. Values of the vibrational amplitudes were determined in the GED experiment (Doms *et al.*, 1983). As can be seen in Table 3 the ratios U_i/S_i are equal for the two normally distributed distances.

The sample corresponding to the C(1)-C(7) distance is not normally distributed, but skewed to larger values. One possible reason (hypothesis) is: the number of derivatives with increased C(1)-C(7) bond length (n_+) is, by accident, larger than the number with decreased C(1)-C(7) bond length (n_-). This implies that the experimental sample with $\bar{x} = 1{\cdot}539$ Å and $S^2 = 3{\cdot}75 \times 10^{-4}$ Å^2 is an unfortunate selection out of the 'true' population, normally distributed around a mean x_o with standard deviation d^2, in which factors enlarging the bond cancel factors shortening it. The behaviour of C(1)-C(2) and C(2)-C(3) distributions with constant U_i/S_i ratio (Table 3) allows one to estimate $d^2[C(1)-C(7); n_+ > n_-]$ as $d^2 = (U_{17}/2{\cdot}53)^2 = 4{\cdot}27 \times 10^{-4}$ Å^2 and then from $d^2 - S^2 = [N/(N-1)](x_0 - \bar{x})^2$ it follows $x_o = 1{\cdot}532$ Å. The behaviour of the variable $(x_i - x_o)^2$, given in Table 4, then allows one to reject the hypothesis that the experimental C(1)-C(7) distribution belongs to the above normal distribution. Hence we must accept that the C(1)-C(7) distribution is skewed by anharmonicity, *i.e.* the mean enlargement is greater than the mean shortening. Therefore, the median value of the distribution is preferred to give a (rather uncertain) estimate of the C(1)-C(7) bond length in the parent hydrocarbon.

Valence angles

The distributions of valence angles (Fig. 4, Table 2) were tested for normality at the 97·5% significance level using contingency tables and the χ^2 test. The

hypothesis H_0: the sample is normally distributed can be rejected for C(1)-C(2)-C(3) and C(2)-C(1)-C(6), but not for C(2)-C(1)-C(7) and C(1)-C(7)-C(4). In particular, the distribution of C(2)-C(1)-C(6) is remarkable, because it is smeared out over a very wide range. Obviously, this angle is much more deformable than the other valence angles. This is probably because C(2)-C(1)-C(6) is the only angle not taking part in a five-membered ring. For the other angles there is a connection between the variance of the sample and the vibrational behaviour of the parent hydrocarbon: the larger bending-force constants accompany the smaller variances.

Torsion angles

The averaging of torsion angles in not as straightforward as for valence angles and distances. The sign of a torsion angle depends upon the absolute configuration, an aspect that is neglected in most of the 51 entries in our sample set. If the mean value of a distribution of torsion angles is large compared to the range, then the absolute value can be taken and analysed in the same way as other internal parameters. Lack of knowledge of the sign becomes fatal when the mean torsion angle is small compared to the range. This is the case for C(1)-C(2)-C(3)-C(4) and therefore the mean absolute value (4·8°) does not have much significance. In compliance with the C_{2v} symmetry imposed on all other parameters, we will impose the value of 0° on C(1)-C(2)-C(3)-C(4).

Geometry of averaged X-ray fragments compared to free norbornane

Median values of the distributions are collected in Table 5 together with results from GED and from completely relaxed *ab initio* calculations. The latter, published by Doms *et al.* (1983), were converted to r_α geometry. All methods produce practically the same overall CC distance (1·546–1·553 Å). We take this as an '*a posteriori*' justification for the hypothesis that in this case $\langle x \rangle \simeq x_g$. It also indicates that systematic differences arising from different measuring temperatures and different refinement schemes used in the X-ray determinations do not play an important role.

The agreement for valence and torsion angles is striking and points to the conclusion that the sequence of valence angles is C(1)-C(7)-C(4) < C(2)-C(1)-C(7) < C(1)-C(2)-C(3) < C(2)-C(1)-C(6). Unfortunately, the agreement for individual bond lengths is less and does not allow C(1)-C(2) and C(1)-C(7) to be placed in sequence.

Table 4. *Contingency table of* $(x_i - x_o)^2$, *and results of* χ^2 *test for the hypothesis that the mean-square lengthening of* C(1)–C(7) *is equal to the mean-square shortening*

Intervals	0 ↓ 1×10^{-4}	1×10^{-4} ↓ 2×10^{-4}	2×10^{-4} ↓ 3×10^{-4}	3×10^{-4} ↓ 4×10^{-4}	4×10^{-4} ↓ 10×10^{-4}	10×10^{-4} ↓ 16×10^{-4}	16×10^{-4} ↓ ∞
Number of distances in sample	43	17	9	13	4	7	10
Number of distances if χ^2 distribution	33·7	15·3	7·1	6·1	22·4	10·2	7·1

$\chi^2 = 30·5$ and $\chi^2(4, 0·95) = 9·5$; thus the hypothesis can be rejected.

Table 5. *Comparison of the geometry of averaged X-ray fragments with the geometry of unsubstituted norbornane*

	X-ray	Electron diffraction	Ab initio
Bond lengths (Å)			
C(1)–C(2)	1·544	1·536	1·545
C(1)–C(7)	1·535	1·544	1·544
C(2)–C(3)	1·559	1·573	1·576
(CC)	1·546	1·547	1·553
Valence angles (°)			
C(1)–C(2)–C(3)	103·0	102·7	103·1
C(2)–C(1)–C(6)	108·2	109·0	108·0
C(2)–C(1)–C(7)	101·8	102·0	101·6
C(1)–C(7)–C(4)	94·3	93·4	94·6
Torsion angles (°)			
C(6)–C(1)–C(2)–C(3)	71·2	−71·6	−71·3
C(2)–C(1)–C(7)–C(4)	55·5	−56·3	−55·7
C(7)–C(1)–C(2)–C(3)	35·1	35·8	35·1
C(1)–C(2)–C(3)–C(4)	4·8	0·0	0·0

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A Revision of van der Waals Atomic Radii for Molecular Crystals: N, O, F, S, Cl, Se, Br and I Bonded to Carbon

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Abstract

The Cambridge Structural Database has been used to determine the effective non-bonding (van der Waals) shapes of N, O, F, S, Cl, Se, Br and I atoms. In all cases these atoms were bonded to a single carbon atom. For O and N, the shapes are virtually spherical but for the remainder, the shape is more or less spheroidal, always having the shorter radius along the atom-to-carbon bond vector ('polar flattening'). The results imply that these effective shapes are transferable from crystal to crystal only so long as the immediate chemical environment of the non-bonded atom is not changed. Some implications for intermolecular force theory are briefly discussed.

Introduction

The non-bonding (van der Waals) atomic radii currently widely used for molecular crystals are taken from tables of Pauling (1942), or that, somewhat