

The mixture was filtered several times and the residue, which remained on the filter paper, was washed with several portions of acetone. The combined filtrates were concentrated on a rotary evaporator and solid material began to form while the concentrated residue was cooling. The product was recrystallized from acetonitrile at 3 °C to give 1.6 g (55%) of *N*-methyl-2-(2-hydroxy-3,3-dimethylbutyl)cyclohexanecarboxamide-¹³C (**8**). ¹³C NMR (CDCl₃) Table IV; ¹H NMR (CDCl₃) δ 3.3-2.7 (m, 5 H), 2.4-1.3 (br), 0.9 (s, 9 H).

cis- and trans-3,4-Dimethyl-4-isopropyl-3-azabicyclo[4.4.0]decan-2-one-2-¹³C (8). One gram (0.004 mol) of *N*-methyl-2-(2-hydroxy-3,3-dimethylbutyl)cyclohexanecarboxamide-¹³C and 20 mL of concentrated sulfuric acid were reacted following the procedure used in the preparation of **6** to give a 0.7 g (80%) mixture of *cis*- and *trans*-3,4-dimethyl-4-isopropyl-3-azabicyclo[4.4.0]decan-2-one-2-¹³C isomers (bp 130-132 °C/5 torr). The mixture of *cis* and *trans* isomers was used without further separations: ¹³C NMR (CDCl₃). Table IV; ¹H NMR (CDCl₃) δ 2.9 (d, 3 H), 2.5-1.3 (br), 1.2 (s, 3 H), 1.1-0.8 (m, 6 H).

2-Pyrrolidone-5-carboxylic-2-¹³C Acid (9). DL-Glutamic-¹³C acid was prepared by the reaction of acrylic-¹³C acid with diethyl acetamidomalonic acid;⁶⁹ DL-glutamic-¹³C acid monohydrate 2.0 g (0.12 mol) in 15 mL of water was sealed in a glass tube, and the solution was heated at 140 °C for 8 h.⁷⁰ After cooling, the solution was eluted with water on a column of Dowex 50H-X8H⁺ ion-exchange resin (30 × 1 cm), and the product was obtained by evaporating the water to give 1.3 g (85%) of 2-pyrrolidone-5-carboxylic-2-¹³C acid (**9**); ¹³C NMR (D₂O) Table IV; ¹H NMR (250 MHz, Me₂SO-*d*₆) δ 7.93 (H1), 4.07 (H5), 2.32 (H4a, 2.14 (H3b), 2.12 (H3a), 1.97 (H4b) (*J* = -13.03 Hz, H4a, H4b), -17.57 (H3a, H3b), 5.46 (H3a, H4b), 9.55 (H3b, H4b), 4.39 (H4b, H5), 9.94 (H3a, H4a), 7.47 (H3b, H4a), 9.16 (H5, H4a), 1.20 (H1, H5), -0.04 (H1, H4b), -0.17 (H3a, H5), -0.58 (H1, H3a), -0.08 (H3b, H5), 0.63 (H1, H3b), 0.11 (H1, H4a).

***N*-(2-Methylbenzoyl)-¹³C proline (10)** was obtained by means of a Schotten-Baumann-type reaction wherein 2-methylbenzoyl chloride was the acylating agent. The procedure is similar to that described by

Davies⁷¹ and Greenstein.⁷² The crude product was recrystallized from aqueous ethanol to give 3.6 g (76.5%) of **10**: mp 152-154 °C NMR (CDCl₃) Table IV; ¹H NMR (250 MHz, CDCl₃) δ 7.25 (m, 4 H), 4.73 (m, 1 H), 3.77 (m, 1 H), 3.25 (m, 2 H), 2.35 (s, 3 H), 2.25 (m, 2 H), 1.97 (m, 2 H); IR (KBr) 2950-2450, 1737, 1608, 1589 cm⁻¹.

***N*-(2-Methylbenzoyl)-2-azabicyclo[2.2.2]octane-carboxyl-¹³C (14a and 14b).** 2-Azabicyclo[2.2.2]octane was prepared by a procedure similar to that of Wilson et al.⁷³ wherein 2-azabicyclo[2.2.2]octan-2-one was reduced with lithium aluminum hydride. One gram of 2-azabicyclo[2.2.2]octane was dissolved in a mixture of 30 mL of benzene and 20 mL of pyridine. To this mixture was added dropwise a solution of 1.4 g (0.009 mol) of *o*-toluoyl-¹³C chloride in 5 mL of benzene. The solution was stirred for 10 h, and the solvent was evaporated under reduced pressure. The residue was dissolved in 100 mL of benzene and was washed with two 30-mL portions of saturated sodium bicarbonate solution, followed by washing with water. After evaporating the benzene, the compound was recrystallized from methanol/water to give 1.4 g (68%) of *N*-(2-methylbenzoyl)-2-azabicyclo[2.2.2]octane-carboxyl-¹³C (**14a** and **14b**); mp 87-88 °C; ¹³C NMR (CDCl₃) Table IV; ¹H NMR (250 MHz, CDCl₃) δ 7.05-7.28 (m, 4 H), 4.65 (m, 2 H, minor isomer), 3.63 (m, 2 H, major isomer), 3.33 (m, 1 H, major isomer), 3.07 (m, 1 H, minor isomer), 2.31 (s, 3 H), 2.05 (m, 1 H), 1.56-1.87 (m, 8 H); IR (KBr) 2946, 2872, 1632, 1605 cm⁻¹. Anal. Calcd for C₁₅H₁₉NO: C, 78.60; H, 8.30; N, 6.11. Found: C, 78.70; H, 8.46; N, 6.12.

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Ultrashort Nonbonded H···H Distance in a Half-Cage Pentacyclododecane

Otto Ermer,^{*1} Sax A. Mason,² Frank A. L. Anet,³ and Steve S. Miura³

Contribution from the Abteilung für Chemie der Ruhr-Universität, D-463 Bochum, Federal Republic of Germany, the Institut Laue-Langevin, 156X, F-38042 Grenoble Cedex, France, and the Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024. Received September 11, 1984

Abstract: A nonbonded H···H distance of only 1.617 (3) Å has been measured by low-temperature neutron diffraction in the pentacyclic half-cage compound **8**, by far the shortest such contact hitherto observed. NMR estimates based on nuclear Overhauser measurements are in satisfactory agreement with the neutron result while empirical force-field calculations with the MM2 potential overestimate the short H···H distance by 0.19 Å. The strong H···H repulsion in **8** leads to an enhanced C-H stretching frequency of 3119 cm⁻¹.

The strain of numerous sterically overcrowded molecular structures originates from short nonbonded H···H contacts. Such structures may correspond to potential energy minima or conformational transition states and frequently the latter involve particularly severe H···H repulsions leading to substantial in-

terconversion barriers. The often unusual and therefore interesting properties of many congested molecules thus depend critically on the nature of nonbonded H···H interactions at short distances. The development of theoretical tools for the computational treatment of overcrowded molecules, in particular empirical force field methods, requires reliable experimental reference data of compounds with short H···H distances on which the calculational models can be tested and calibrated. Obviously, a key property of overcrowded molecules concerns the short nonbonded contacts

(1) Ruhr-Universität.

(2) Institut Laue-Langevin.

(3) University of California, Los Angeles.

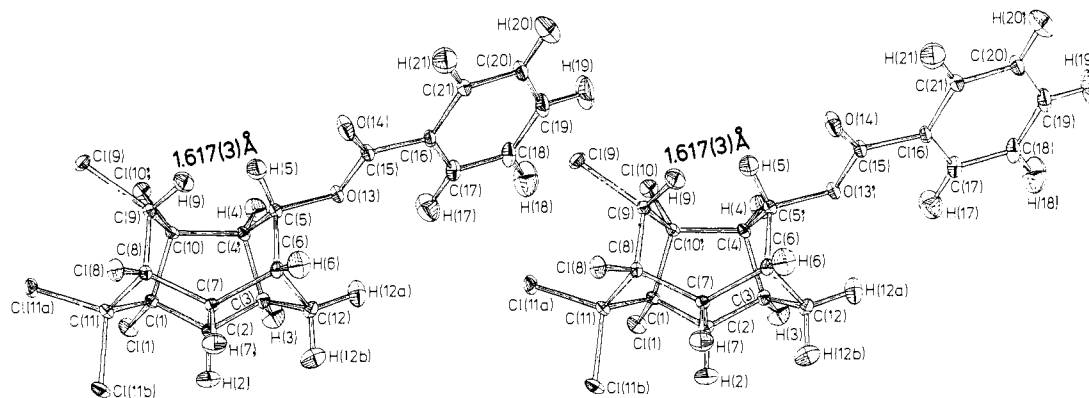
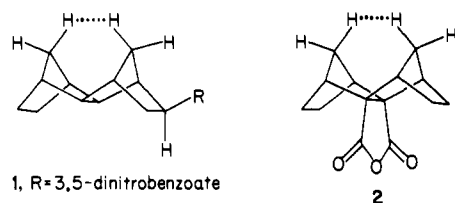


Figure 1. Structure of **8** observed by neutron diffraction at 113 (1) K. Stereoview with thermal ellipsoids (50%) and atomic numbering.

themselves and we report here the reliable experimental determination of an extremely short nonbonded H...H distance.

As is well-known, hydrogen positions obtained from X-ray measurements suffer from large random and systematic errors because the X-ray scattering power of the hydrogen atom is relatively small and its electron density maximum usually does not coincide with the proton location, respectively. In C-H bonds the hydrogen electron density maximum is shifted by about 0.1 Å toward the bound carbon atom such that X-ray C-H bond lengths are usually too short by this amount ("foreshortening"). On the other hand, neutron diffraction is free from these disadvantages since the neutrons are scattered at the nuclei and the respective scattering powers of hydrogen and heavier atoms differ much less than in the case of X-rays which are scattered at the electrons.

Recently, reliable low-temperature single-crystal neutron diffraction measurements have been reported for the derivatives **1** and **2** of *exo,exo*-tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecane which gave very short nonbonded (internuclear) H...H distances of only 1.754 (4) and 1.713 (3) Å, respectively, between the inner hydrogen atoms of the congested methylene bridges.⁴ The corresponding

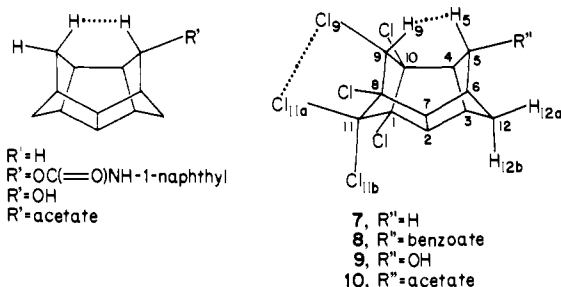


1, R = 3,5-dinitrobenzoate

2

calculated H...H distances obtained with a consistent force field (CFF)⁵ and Allinger's MM2 potential⁶ are about 0.14 Å larger and it was concluded accordingly that the nonbonded H...H functions of these force fields are too strongly repulsive at short distances.

Pentacyclo[6.2.1.1^{3,6}.0^{2,7}.0^{4,10}]dodecane **3**⁷ is another polycyclic



3, R' = H
4, R' = OC(=O)NH-1-naphthyl
5, R' = OH
6, R' = acetate

7, R'' = H
8, R'' = benzoate
9, R'' = OH
10, R'' = acetate

hydrocarbon made up of fused norbornane units which has a very

short inner H...H contact. The crystal structure of the derivative **4** has recently been determined at room temperature by X-ray methods and the short H...H distance was measured as 1.82 (4) Å.⁸ The average length of the two inner C-H bonds involved in this close nonbonded contact resulted as only 0.96 (3) Å. Correcting for the foreshortening by normalizing both C-H bond lengths to the neutron diffraction value, 1.089 (3) Å,⁴ of the analogous bonds in **1** allows estimation of the internuclear short H...H distance in **4** at 1.70 Å. The calculated values for the mirror-symmetric half-cage hydrocarbon **3** of 1.887 (CFF)⁵ and 1.912 Å (MM2), respectively, are again substantially larger. (MM2 calculations for the half-cage alcohol **5** and the acetate **6** gave somewhat shorter values of 1.886 and 1.878 Å, respectively.)

Model considerations suggest that the inner H...H contact of the hexachloro half-cage compound **7**⁹ should be still shorter than in the parent half-cage hydrocarbon **3** since the chlorine atoms Cl(9) and Cl(11a) approach each other rather closely and the resulting nonbonded Cl...Cl repulsion tends to push the group Cl(9)-C(9)-H(9) inward toward H(5) essentially in the sense of a rocking deformation (see formula sketch and Figure 1). A recent low-temperature (113 K) X-ray analysis of the derivative **8**¹⁰ indeed furnished an inner H...H distance of only 1.78 (5) Å and a foreshortening correction similar to that for **4** yields an estimate of as low as 1.64 Å for the internuclear short H...H distance in **8**. (The average X-ray value for the two inner C-H bond lengths in **8** is 0.93 (4) Å.¹⁰) The MM2 calculated values for the hexachloro half-cage hydrocarbon **7**, the alcohol **9**, and the acetate **10** are 1.851, 1.807, and 1.805 Å, respectively. The substantial computational overestimation of the short inner H...H distances thus appears similar for the half-cage and hexachloro half-cage compounds; expectedly, the oxygen substitution at C(5) seems to effect a larger additional H...H shortening in the more extreme hexachloro derivatives as a consequence of a repulsive O...H interaction with H(12a). It is noted that a force field based on the hydrocarbon parameters of Boyd¹¹ and the chlorine constants of Meyer and Allinger¹² gives an inner H...H distance of 1.65 Å for **7**,¹³ considerably shorter than the MM2 estimate.

Another piece of evidence concerning the short H...H contact in the hexachloro half-cage has been derived from NMR measurements (nuclear Overhauser enhancements), and the short internuclear H...H distance of the acetate **10** was estimated at 1.60 (5) Å in this way.¹³ (Similar NMR measurements gave 1.76–1.79 Å for the chlorine-free alcohol **5**.¹⁴) However, the derivation of internuclear distances from NMR data involves assumptions about nuclear relaxation mechanisms and an inde-

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Table I. Fractional Atomic Nuclear Coordinates ($\times 10^5$) and Anisotropic Temperature Factor Coefficients ($\text{\AA}^2 \times 10^4$) of **8** with Estimated Standard Deviations in Parentheses^a

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
C(1)	29 507 (7)	10 224 (9)	46 724 (8)	78 (4)	111 (4)	110 (4)	-22 (3)	10 (3)	6 (3)
C(2)	24 775 (8)	608 (9)	53 592 (8)	106 (4)	97 (4)	107 (3)	5 (3)	-3 (3)	8 (3)
C(3)	25 245 (8)	5 252 (10)	64 287 (8)	99 (4)	138 (4)	100 (4)	6 (3)	-15 (4)	5 (4)
C(4)	22 561 (7)	19 451 (9)	62 735 (7)	105 (4)	110 (4)	88 (4)	-27 (3)	9 (4)	-16 (3)
C(5)	11 356 (8)	19 428 (10)	64 814 (7)	96 (4)	128 (4)	88 (4)	-18 (3)	17 (3)	-1 (4)
C(6)	8 673 (8)	5 984 (9)	61 385 (7)	91 (4)	125 (4)	90 (4)	4 (3)	2 (4)	-24 (4)
C(7)	13 429 (7)	2 299 (9)	50 978 (8)	97 (4)	82 (4)	99 (4)	-11 (3)	0 (4)	-18 (3)
C(8)	13 623 (8)	11 151 (9)	41 460 (7)	91 (4)	111 (4)	76 (3)	1 (3)	0 (3)	0 (3)
C(9)	15 162 (7)	24 617 (9)	45 165 (7)	100 (4)	97 (4)	100 (3)	3 (3)	15 (3)	3 (3)
C(10)	24 947 (7)	22 781 (9)	51 401 (7)	91 (4)	87 (4)	104 (4)	-20 (3)	17 (4)	-5 (3)
C(11)	23 884 (8)	7 732 (10)	36 886 (7)	114 (4)	123 (4)	100 (3)	-25 (3)	20 (4)	8 (4)
C(12)	15 883 (8)	-1 226 (10)	68 365 (8)	153 (5)	133 (4)	109 (4)	29 (4)	-3 (4)	-17 (4)
O(13)	10 082 (9)	20 556 (11)	75 545 (9)	120 (5)	176 (5)	86 (4)	-18 (4)	16 (4)	5 (4)
O(14)	-5 271 (11)	28 181 (16)	73 043 (10)	156 (6)	408 (8)	122 (5)	2 (5)	16 (5)	102 (6)
C(15)	1 301 (8)	25 130 (11)	78 664 (7)	123 (5)	163 (4)	81 (3)	-7 (4)	14 (4)	5 (4)
C(16)	726 (8)	26 055 (10)	89 740 (7)	149 (5)	137 (4)	80 (3)	-6 (4)	25 (4)	-14 (4)
C(17)	8 040 (9)	21 193 (12)	96 036 (8)	163 (5)	223 (5)	107 (4)	15 (4)	-1 (4)	-21 (4)
C(18)	7 200 (10)	22 670 (13)	106 373 (8)	225 (6)	308 (7)	100 (4)	18 (4)	4 (4)	-56 (5)
C(19)	-845 (10)	29 159 (12)	110 402 (9)	290 (6)	265 (6)	97 (4)	-23 (4)	54 (4)	-68 (5)
C(20)	-8 191 (10)	33 918 (12)	104 146 (9)	287 (6)	197 (5)	130 (4)	-23 (4)	94 (5)	-1 (5)
C(21)	-7 438 (9)	32 294 (11)	93 829 (8)	199 (5)	147 (4)	123 (4)	0 (4)	59 (4)	12 (4)
Cl(1)	42 375 (5)	9 249 (8)	45 863 (6)	79 (3)	232 (4)	221 (3)	-34 (3)	26 (3)	12 (3)
Cl(8)	3 486 (6)	9 149 (8)	33 384 (6)	128 (3)	236 (4)	110 (3)	-8 (3)	-40 (3)	-20 (3)
Cl(9)	15 057 (6)	36 716 (7)	35 929 (6)	194 (4)	138 (3)	165 (3)	67 (3)	46 (3)	37 (3)
Cl(10)	32 883 (6)	35 984 (7)	50 747 (7)	164 (3)	138 (3)	205 (3)	-18 (3)	34 (3)	-79 (3)
Cl(11a)	28 166 (6)	16 558 (8)	26 614 (6)	174 (3)	221 (4)	117 (3)	22 (3)	66 (3)	16 (3)
Cl(11b)	24 369 (6)	-8 244 (7)	33 027 (6)	232 (4)	146 (3)	162 (3)	-75 (3)	16 (3)	22 (3)
H(2)	27 558 (19)	-8 934 (21)	52 419 (19)	321 (12)	162 (9)	302 (11)	-6 (9)	6 (10)	61 (8)
H(3)	32 260 (18)	3 619 (25)	68 133 (19)	195 (10)	369 (12)	251 (10)	10 (10)	-94 (9)	41 (10)
H(4)	26 634 (19)	25 819 (24)	67 645 (17)	257 (11)	278 (11)	231 (9)	-76 (9)	-17 (9)	-91 (9)
H(5)	6 980 (18)	27 122 (22)	61 642 (17)	266 (11)	260 (11)	193 (9)	19 (8)	18 (9)	85 (9)
H(6)	775 (17)	3 690 (24)	61 977 (19)	162 (10)	321 (12)	280 (11)	-1 (9)	13 (9)	-69 (9)
H(7)	10 153 (18)	-6 669 (21)	48 606 (18)	274 (11)	177 (9)	276 (10)	-40 (8)	-17 (9)	-61 (8)
H(9)	8 917 (16)	27 276 (21)	49 710 (18)	183 (10)	254 (10)	221 (9)	4 (8)	47 (9)	54 (8)
H(12a)	14 459 (19)	196 (26)	76 359 (17)	311 (12)	376 (13)	158 (9)	23 (9)	27 (9)	-1 (10)
H(12b)	16 050 (21)	-11 369 (21)	66 742 (20)	374 (13)	177 (9)	344 (13)	31 (9)	12 (11)	-19 (10)
H(17)	14 338 (22)	16 233 (32)	92 840 (21)	298 (13)	524 (17)	261 (12)	-4 (12)	2 (11)	103 (13)
H(18)	12 857 (24)	18 884 (38)	111 340 (22)	377 (16)	743 (23)	245 (12)	74 (14)	-74 (12)	10 (16)
H(19)	-1 290 (27)	30 453 (34)	118 516 (19)	591 (20)	598 (20)	137 (9)	-25 (12)	94 (11)	-37 (16)
H(20)	-14 448 (25)	39 009 (32)	107 209 (23)	474 (18)	481 (18)	344 (14)	-60 (13)	175 (14)	137 (15)
H(21)	-13 064 (22)	35 907 (28)	88 822 (21)	341 (14)	402 (15)	300 (12)	47 (11)	31 (11)	120 (12)

^a $f = f^0 \exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{23}klb^*c^* + \dots)]$. **8** crystallizes in the polar space group *Pna2*₁. Since the parameters of two groups of atoms were fixed alternatively in the refinements, estimated standard deviations are given for all positional parameters.

pendent reliable experimental determination of the extraordinarily short proton-proton distance in the hexachloro half-cage is desirable. The verification of the NMR estimate appears to be of interest also in a more general context since nuclear Overhauser experiments are of growing importance as a unique tool for quantitative structural measurements in solution.¹⁵ In the following, we report the results of a low-temperature neutron diffraction measurement on the crystalline hexachloro half-cage benzoate **8** which furnished reliable hydrogen nuclear positions (note the superiority of neutron over X-ray diffraction in the present example also as regards the presence of the six rather heavy chlorine atoms). Detailed accounts on the combined NMR, X-ray, and force field analysis of hexachloro half-cage compounds¹⁰ and a X-ray/force field study of the chlorine-free system⁸ will appear separately. The present neutron diffraction study thus serves the threefold purpose of evaluating the force field, X-ray, and NMR estimates of the short H...H contact. The half-cage moiety is sufficiently rigid (lowest calculated vibrational frequency of **3**, 207 cm⁻¹)⁵ such that intermolecular effects like crystal packing forces are likely to be of minor importance and may be neglected

in the various structural comparisons.

Experimental Section

Large crystals of **8** could be grown from methanol solution. *Crystal data*: orthorhombic, space group *Pna2*₁, *Z* = 4, *a* = 13.520 (3) Å, *b* = 10.639 (5) Å, *c* = 13.369 (4) Å (cell constants taken over from the X-ray study¹⁰). Neutron intensities of totally 3792 reflections were measured at 113 (1) K (same temperature as in the X-ray measurement) on the four-circle diffractometer D9 at the high-flux beam reactor of the Institut Laue-Langevin, Grenoble, at a wavelength of 0.8402 (2) Å using a crystal of 12 mm³ volume. After averaging, 3373 independent intensities remained; the 3290 reflections with observed intensities (*I* > 0) were included in the least-squares refinement. Absorption corrections were applied with a respective coefficient of 1.28 cm⁻¹ (incoherent scattering cross section of hydrogen taken as 35 b). The final *R* value after anisotropic refinement was 0.029 (*R*_w = 0.021, $\sum w(\Delta F)^2$ minimized, $w = 1/\sigma(F_o)^2$, empirical extinction correction, neutron scattering lengths taken from a recent compilation of the International Atomic Energy Agency,¹⁶ crystallographic calculations with SHELX76¹⁷). The refined atomic nuclear coordinates and anisotropic temperature factor coefficients are listed in Table I and a stereoview of the molecule with thermal ellipsoids (50% probability) and the atomic numbering is shown in Figure 1. Observed and calculated geometrical key parameters involving the congested groups H(9)-C(9)-Cl(9) and H(5)-C(5)-O(13) are collected in Table II while in Figure 2 pictorial comparisons are made between various half-cage structures. A list of observed and calculated neutron structure amplitudes is available as supplementary material.

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Table II. Comparison of Observed and Calculated Nonbonded Distances (Å), Bond Lengths (Å), and Bond Angles (deg) Involving the Congested (Substituted) Methylene Groups of the Hexachloro Half-Cage Compounds **8**, **9**, and **7**

	8		calcd (MM2)	
	obsd in crystal (neutron diffractn)		9	7
H(5)...H(9)	1.617 (3)		1.807	1.851
C(5)...C(9)	2.733 (2)		2.810	2.793
Cl(9)...Cl(11a)	3.048 (1)		3.042	3.058
O/H(13)...H(12a)	2.248 (3)		2.373	2.166
C(5)-H(5)	1.095 (3)		1.110	1.110
C(5)-O/H(13)	1.450 (2)		1.422	1.116
C(9)-H(9)	1.078 (3)		1.101	1.102
C(9)-Cl(9)	1.784 (1)		1.801	1.800
H(5)-C(5)-O/H(13)	104.9 (2)		101.5	100.0
H(5)-C(5)-C(4)	117.4 (2)		117.4	117.8
H(5)-C(5)-C(6)	116.8 (2)		116.0	118.2
O/H(13)-C(5)-C(4)	107.2 (1)		110.0	110.5
O/H(13)-C(5)-C(6)	110.0 (1)		113.5	111.1
C(4)-C(5)-C(6)	100.3 (1)		98.9	99.6
H(9)-C(9)-Cl(9)	101.2 (2)		97.0	97.8
H(9)-C(9)-C(10)	113.1 (2)		117.8	117.4
H(9)-C(9)-C(8)	108.8 (2)		108.4	108.3
Cl(9)-C(9)-C(10)	117.5 (1)		118.0	117.9
Cl(9)-C(9)-C(8)	116.8 (1)		117.0	116.7
C(8)-(9)-C(10)	99.8 (1)		99.2	99.3

Discussion

The present neutron diffraction measurement gives the reliable value of 1.617 (3) Å for the internuclear inner H(5)...H(9) separation of the hexachloro half-cage benzoate **8** (Table II). This extremely short nonbonded H...H distance is by far the shortest hitherto measured. The substantial shortening with respect to the above-mentioned X-ray value of 1.78 (5) Å¹⁰ is almost entirely due to the foreshortening of the inner congested C-H bonds (Figure 2a): The neutron lengths of the bonds C(5)-H(5) and C(9)-H(9) are 1.095 (3) and 1.078 (3) Å, respectively, compared to the X-ray values of only 0.90 (4) and 0.97 (4) Å, respectively.¹⁸ Within the experimental uncertainties of the X-ray result, we may therefore conclude that also in C-H bonds under serious nonbonded pressure of the kind realized in the present fused norbornane systems the electron density maximum of the hydrogen atom is shifted toward the bound carbon atom essentially in the same way as in normal nonbonded C-H bonds, i.e., along the line connecting both nuclei. The previous X-ray and neutron diffraction study of **1** led to the same conclusion.^{4,5,19,20} The internuclear H(5)...H(9) distance of 1.64 Å estimated from the X-ray measurement of **8** (see above) therefore turns out to be a rather good guess. Likewise, the NMR estimate of 1.60 (5) Å¹³ referred to in the introduction is satisfactory and the theoretical (relaxation) model it rests upon thus appears reasonable.¹⁰

The structural comparison between the inner congested (substituted) methylene groups of the chlorine-free half-cage derivative **4** and the present hexachloro compound **8** (Figure 2b) shows that the shorter H...H distance of **8** is mainly due to an inward rocking deformation of the group H(9)-C(9)-Cl(9) induced by the short nonbonded Cl(9)...Cl(11a) contact (3.048 (1) Å as compared to

(18) The rather large foreshortening of the inner congested C-H bonds of **8** (and also of **4**; see introduction) is not unexpected considering the strong nonbonded H...H repulsion and would be in line with the observed magnetic deshielding of the inner hydrogen atoms in half-cage compounds (Winstein, S.; Carter, P.; Anet, F. A. L.; Bourn, A. J. R. *J. Am. Chem. Soc.* **1965**, *87*, 5247. Anet, F. A. L.; Bourn, A. J. R.; Carter, P.; Winstein, S. *Ibid.* **1965**, *87*, 5249). Unfortunately, the limited respective X-ray accuracy precludes more definite conclusions.

(19) Ermer, O. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 798.

(20) The X-ray measurement of **2** (Bartlett, P. D.; Blakeney, A. J.; Kimura, M.; Watson, W. H. *J. Am. Chem. Soc.* **1980**, *102*, 1383) gave an inner H...H distance of 1.68 (9) Å, which is shorter than the neutron value⁴ of 1.713 (3) Å. However, the limited quality of the X-ray study does not allow a meaningful comparison in this case; for example, several H-C-H angles assume unreasonable values including that of one methylene bridge apparently resulting from a misplaced inner congested hydrogen atom.

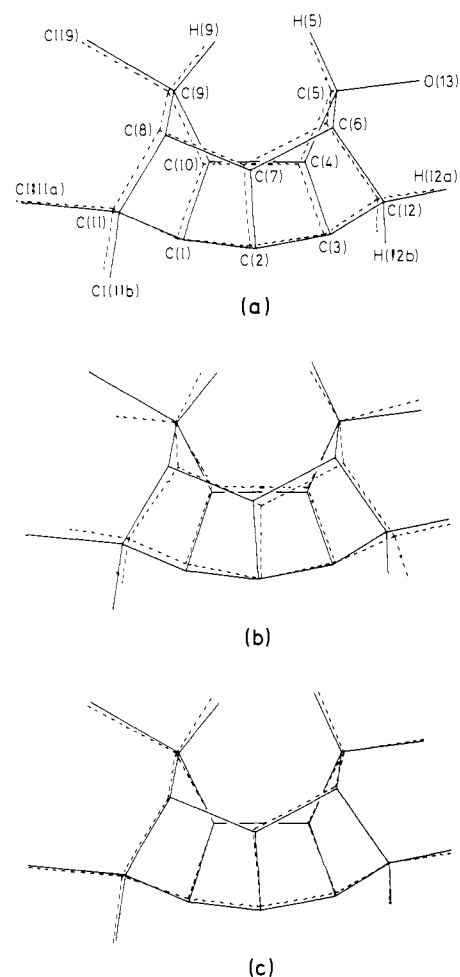


Figure 2. Pictorial comparisons between various observed and calculated half-cage structures. The projections are on to the planes running through C(5) and C(9) and bisecting the improper torsion angle H(5)-C(5)...C(9)-H(9). The midpoints of C(5)...C(9) are made to coincide except for a shift of 0.1 Å along C(5)...C(9) in (a) in order to avoid obscuring overlap. The structure given with full lines is in all three cases that of **8** observed by neutron diffraction. The origin of the compared (dashed) structures is (a) X-ray of **8**, (b) X-ray of **4**, and (c) MM2 calculation of **9**.

a standard van der Waals distance of 3.60 Å²¹). Apparently, this H-C-Cl inward rock is facilitated by appreciable distortions from mirror symmetry of the pentacyclic carbon skeleton¹⁰ (Figure 2b), which occur despite its relative rigidity (see above). The structural response of the group H(5)-C(5)-O(13) to the increased nonbonded pressure in **8** is an additional outward rocking deformation relative to **4** which is smaller, however, than the inward rock at C(9) since an opposing nonbonded repulsion between O(13) and H(12a) comes into play (Figure 2b). A more quantitative picture of these deformations in **8** may be derived from the bond angles at C(5) and C(9) given in Table II. Expectedly, the bonds C(5)-H(5) and C(9)-H(9) are compressed; the amount of about 0.01-0.02 Å is relatively small, however, because both bonds are far from being colinear. Obviously, the angles H(9)-C(9)-Cl(9) and H(5)-C(5)-O(13) are also smaller than normal (Table II), in particular the former, which is under more severe nonbonded pressure.

The MM2 force field gives a short inner H...H distance of 1.807 Å for the hexachloro half-cage alcohol **9**, i.e., 0.190 Å longer than the observed neutron value, 1.617 (3) Å, of **8**. This rather large discrepancy (corresponding to an estimated nonbonded H...H interaction energy difference of no less than about 7 kcal mol⁻¹ concentrated in just one degree of freedom!) is paralleled by the

(21) Pauling, L. "The Nature of the Chemical Bond"; Cornell University Press: Ithaca, NY, 1939, 1940, 1960.

computational overestimation of the compression of the bond angles H(5)-C(5)-O(13) and H(9)-C(9)-Cl(9) and by the exaggerated calculated nonbonded distance C(5)···C(9) (Table II, Figure 2c). A similar pattern of deviations between experiment and calculations has been found previously for **1** and **2**.⁴ The results of the neutron diffraction measurement on **8** therefore indicate again an excessive hardness at short distances of the nonbonded H···H potential used in the MM2 force field. On the other hand, it is noteworthy that the short Cl(9)···Cl(11a) distance of 3.042 Å calculated for **9** agrees well with the value of 3.048 (1) Å observed for **8** (Table II).

The severe H···H repulsions in the present fused norbornane compounds are also reflected through unusual increased C-H stretching (ν_{CH}) frequencies as has been found by Winstein et al.²² more than 20 years ago. These frequency enhancements occur for those normal modes that involve simultaneous stretching and compression, respectively, of the inner congested C-H bonds.^{5,22} In keeping with the extraordinarily short inner H···H distance, the largest measured (IR, KBr disk) ν_{CH} frequency of **8** has the very high value of 3119 cm⁻¹ and may be assigned to synchronous inner C-H stretchings (methine ν_{CH} of 2-chloropropane for comparison, 2962 cm⁻¹).^{23,24} Expectedly, the largest ν_{CH} frequency of the less congested chlorine-free half-cage is smaller (IR value of **5**, 3048 cm⁻¹), although still markedly enhanced as compared to the corresponding norbornane frequency (2950-2965 cm⁻¹).^{25,26,28d}

(22) Kivelson, D.; Winstein, S.; Bruck, P.; Hansen, R. L. *J. Am. Chem. Soc.* **1961**, *83*, 2938.

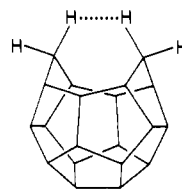
(23) McKean, D. C.; Saur, O.; Travert, J.; Lavalley, J. C. *Spectrochim. Acta, Part A* **1975**, *31A*, 1713.

(24) In order to avoid any confusion that might arise from the aromatic ν_{CH} frequencies of **8**, the IR spectrum of the corresponding hexachloro half-cage propionate was recorded in addition (CCl₄ solution), which also shows a band at 3119 cm⁻¹.

(25) Meič, Z.; Randić, M.; Rubčić, A. *Croat. Chem. Acta* **1974**, *46*, 25. Brunel, Y.; Coulombeau, C.; Coulombeau, C.; Moutin, M.; Jobic, H. *J. Am. Chem. Soc.* **1983**, *105*, 6411.

(26) Similarly, the largest (enhanced) ν_{CH} frequency of the *exo,exo*-tetracyclododecane hydrocarbon underlying **1** (3052 cm⁻¹)²² is smaller than that of the anhydride derivative **2** (3078 cm⁻¹; IR, KBr disk) whose inner H···H distance is shorter. It is noted that the CFF underestimates the ν_{CH} enhancements in this class of compounds since a simple harmonic C-H stretching function is used rather than a more realistic anharmonic potential, e.g., a Morse function.^{5,27,28d} The present fused norbornane compounds also display enhanced δ_{CH_2} scissoring frequencies which involve simultaneous opening and compression, respectively, of the H-C-H angles of the inner congested methylene groups. The CFF overestimates these δ_{CH_2} enhancements considerably, mainly due to the excessive hardness of the nonbonded H···H potential used.^{5,27,28d}

It is tempting to speculate about unusual chemical consequences of the close proximity of the inner congested hydrogen atoms in the present fused norbornane systems. Paquette et al. found that secododecahedrane **11** (and a methyl derivative), which involves



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two topologically similar congested methylene groups (X-ray H···H distance of a dimethyl derivative, 1.95 (11) Å;^{28b} calculated with the CFF, 1.884 Å⁵), may be catalytically dehydrogenated to form dodecahedrane under unusually mild conditions (Pd/C, 250 °C).^{28a} It is conceivable that the fused norbornane compounds display a similar behavior although according to force field calculations the thermodynamic driving force for the replacement of the pair of congested hydrogen atoms by a C-C bond is expected to be smaller (lower strain release) than for secododecahedrane/dodecahedrane.

Acknowledgment. Financial support of the Fonds der Chemischen Industrie is gratefully acknowledged.

Registry No. **8**, 95193-11-6.

Supplementary Material Available: Observed and calculated neutron structure amplitudes for **8** (14 pages). Ordering information is given on any current masthead page.

(27) Ermer, O.; Ivanov, P. M.; Ōsawa, E., manuscript in preparation.

(28) (a) Paquette, L. A.; Ternansky, R. J.; Balogh, D. W.; Kentgen, G. *J. Am. Chem. Soc.* **1983**, *105*, 5446. Paquette, L. A.; Ternansky, R. J.; Balogh, D. W.; Taylor, W. J. *Ibid.* **1983**, *105*, 5441. (b) Christoph, G. G.; Engel, P.; Usha, R.; Balogh, D. W.; Paquette, L. A. *Ibid.* **1982**, *104*, 784. (c) Paquette, L. A.; Balogh, D. W. *Ibid.* **1982**, *104*, 774. (d) It is noted that secododecahedrane **11** as well as a monomethyl- and a dimethylsecododecahedrane show enhanced ν_{CH} frequencies which are likely to arise from the H···H repulsions between the congested methylene groups and whose normal coordinates are characterized by synchronous stretchings of the inner methylene C-H bonds. However, the reported ν_{CH} frequencies of 3030,^{28a} 3020,^{28a} and 3150 cm⁻¹,^{28c} respectively, for these three cage molecules are not consistent. The frequency of 3150 cm⁻¹ for the dimethyl derivative really appears too high; a printing error might have interfered and the correct value could be 3050 cm⁻¹ (?). The CFF gives a calculated largest ν_{CH} frequency of 2985 cm⁻¹ for secododecahedrane **11**,⁵ again smaller than observed as in the case of the fused norbornane systems.^{5,26}

Molecular Dynamics of a Peptide Chain, Studied by Intramolecular Excimer Formation

R. Goedeweck, M. Van der Auweraer, and F. C. De Schryver*

Contribution from the Department of Chemistry, K. U. Leuven, Celestijnenlaan 200 F, B-3030 Heverlee, Belgium. Received June 27, 1984

Abstract: Both diastereomers of the dipeptide *N*-acetylbis(1-pyrenylalanine) methyl ester were studied by means of stationary and transient fluorescence measurements as model compounds of the random-coiled peptide chain. The diastereomeric differences and the solvent influences could be correlated with the populations of two sets of ground-state conformations: an extended conformation, unable to form an excimer, in equilibrium with a folded conformation which does allow a transition to the excimer geometry within the lifetime of an excited pyrene moiety. A consecutive kinetic scheme was used to calculate some relevant kinetic and thermodynamic parameters. Conformational populations have been calculated in toluene (high folded population) and ethyl acetate (high extended population). The conformational equilibrium of the three diastereomer is shifted to the extended conformation, compared with the erythro diastereomer in the same solvent, because of the larger steric hindrance between the amino acid side groups in the three folded conformation.

During several decades, the study of protein luminescence has been limited to the detection of the intrinsic fluorescence of the

natural aromatic amino acids¹ or the extrinsic emission of artificial probes, adsorbed or bound covalently at the protein.² Often, a