Extremely Short Non-bonded H . . . H Distances in Two Derivatives of *exo, exo*-Tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecane

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Non-bonded H · · · H distances of 1.754(4) and 1.713(3) Å have been measured by low-temperature neutron diffraction experiments on the crystals of *exo,exo*-tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecan-4-yl 3′,5′-dinitrobenzoate (2) and *exo,exo*-tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecane-2,7-dicarboxylic anhydride (3); empirical force field calculations for parent gaseous hydrocarbons give larger values by about 0.14 Å.

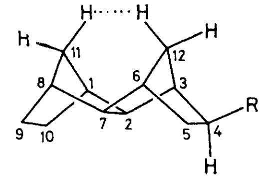
Potential energy terms representing non-bonding interactions are of crucial importance for the success of empirical force field calculations. However, such interactions are not well understood theoretically, and the usual pairwise isotropic atom–atom potentials describing them are merely simple approximate analytical models whose performance has to be verified by comparison with experimental evidence.[1] Experimental structural information on compounds with short non-bonded contacts is useful for calibration of the parameters of non-bonded potentials in the repulsion region.

The three stereoisomers of tetracylo[6.2.1.1^{3,6}.0^{2,7}]dodecane contain short non-bonded H . . . H contacts, in particular the *exo,exo*-isomer (**1**).[2,3] Room temperature *X*-ray crystal structure analyses have been reported earlier for the derivatives (**2**)[2,3] and (**3**).[4] However, the hydrogen positions thus derived suffer from large random and systematic errors due to the limitations of *X*-ray diffraction. We have therefore performed low temperature neutron diffraction measurements on (**2**) and (**3**) in order to obtain more reliable hydrogen positions.

Crystals of (**2**) were grown from chloroform–n-propanol mixtures. Cell constants and neutron intensities were measured at 120(1) K on the four-circle diffractometer D9 at the high-flux beam reactor of the Institut Laue-Langevin (I.L.L.), Grenoble, using a crystal with a volume of 9.1 mm^3. *Crystal data:* monoclinic, space group Pc, $Z = 2$, $a = 13.888(3)$, $b = 5.794(1)$, $c = 10.724(2)$ Å, $\beta = 101.89(2)°$. 3036 Independent intensities were measured at a wavelength $\lambda = 0.8442(2)$ Å and corrected for absorption ($\mu = 1.66$ cm^{-1}). 3009 Reflections with non-zero intensities were included in the least-squares refinement {$R = 0.027$, $R_w = 0.021$; $\Sigma w(\Delta F)^2$ minimized; $w = 1/[\sigma(F_o)]^2$; empirical extinction correction}.†

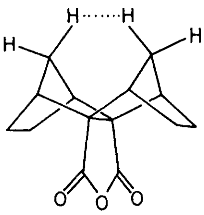
Compound (**3**) was crystallized from acetone–n-hexane mixtures and the neutron measurements were performed at 90(1) K on the diffractometer D8 also at the I.L.L. using a crystal of volume 27.2 mm^3. *Crystal data:* orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 11.727(2)$, $b = 12.706(3)$, $c = 7.346(1)$ Å. 2932 Independent intensities were measured [$\lambda = 0.8964(2)$ Å] and corrected for absorption ($\mu = 1.90$ cm^{-1}). The refinement conditions were the same as for (**2**) (2873 reflections, $R = 0.032$, $R_w = 0.026$).†

Figures 1 and 2 show views of the structures of (**2**) and (**3**) respectively, with thermal ellipsoids (50% probability) and relevant atomic numbering. Table 1 contains geometrical data for the congested methylene groups both from the neutron diffraction experiments on (**2**) and (**3**) and from empirical force field calculations for gaseous *exo, exo*-tetracyclo[6.2.1.1^{3,6}.0^{2,7}]-dodecane (**1**) and compound (**4**). The latter molecule represents the isoconjugate hydrocarbon of (**3**). Force field calculations for (**3**) itself were unobtainable owing to the lack of relevant parameters for the anhydride group. Our consistent force field (CFF)[5] and the MM2 force field[6] were applied for the calculations.

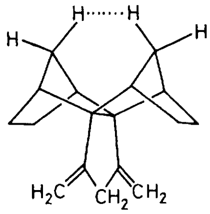


(**1**) R = H

(**2**) R = 3,5-dinitrobenzoate



(**3**)



(**4**)

Despite the strong inner H . . . H repulsion, the tetracyclododecane moieties in (**2**) and compound (**3**) as a whole have, to a good approximation, C_{2v} symmetry in the present crystal structures. This is, in part, due to geometrical rather than energetic factors.[2] The observed short inner H . . . H distances are 1.754(4) Å in (**2**) and 1.713(3) Å in (**3**). These are the shortest internuclear non-bonded H . . . H distances measured so far. As expected, the two methylene groups at C(11) and C(12) involved in the short H . . . H contacts deviate from local C_{2v} symmetry by an outward rocking deformation (Table 1). The H–C–H angles of these groups, though, are by comparison, little compressed. The inner C–H bonds of the two congested methylene groups are about 0.01 Å shorter than the outer.

The two force fields applied give similar results as to the separations of the congested methylene groups in (**1**) and (**4**). The H(111) . . . H(121) distances are longer by about 0.14 Å and 0.13 Å using consistent and MM2 force fields respectively, than those observed for (**2**) and (**3**) (Table 1). Such large differences at such short H . . . H distances, *i.e.* in a very steep region of the corresponding non-bonded potential, cannot be explained with packing forces and/or substituent effects. Thus it appears that the non-bonded H . . . H potentials of both force fields are too strongly repulsive at short distances.

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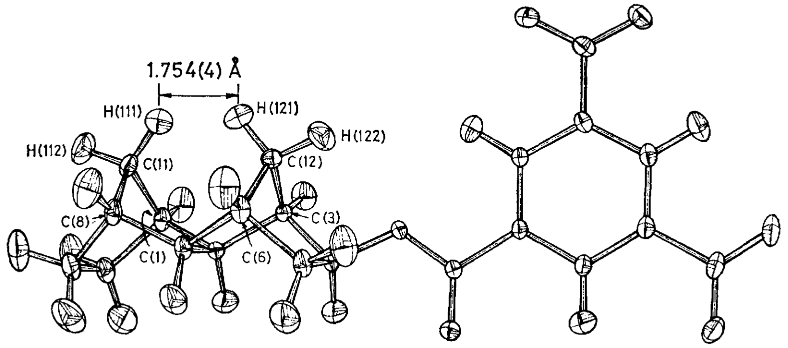
† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Table 1. Bond lengths and angles (both observed and calculated) for the congested methylene groups in compounds (**1**—**4**).[a]

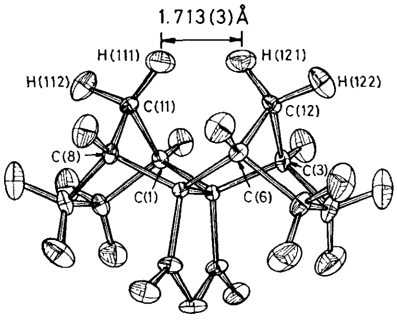
	(**2**) observed in crystal (neutron diffraction)	(**1**) calculated gas phase C_{2v}		(**3**) observed in crystal (neutron diffraction)	(**4**) calculated gas phase C_{2v}	
		CFF	MM2		CFF	MM2
H(111) . . . H(121)	1.754Å	1.899	1.890	1.713	1.854	1.837
C(11) . . . C(12)	3.112	3.216	3.209	3.068	3.166	3.158
C(11)-H(111)	1.088	1.095	1.106	1.091	1.092	1.104
C(12)-H(121)	1.089			1.085		
C(11)-H(112)	1.096	1.108	1.116	1.099	1.109	1.117
C(12)-H(122)	1.103			1.101		
H(111)-C(11)-H(112)	107.6°	109.8	105.9	107.5	108.6	104·3
H(121)-C(12)-H(122)	108.1			107.6		
H(111)-C(11)-C(1)	115.4	115.3	115.7	116.2	116.0	116.5
H(111)-C(11)-C(8)	115.8			116.8		
H(121)-C(12)-C(3)	115.1			115.8		
H(121)-C(12)-C(6)	115.4			116.8		
H(112)-C(11)-C(1)	111.7	111.4	113.4	110.5	111.5	113.7
H(112)-C(11)-C(8)	111.5			110.3		
H(122)-C(12)-C(3)	111.4			111.0		
H(122)-C(12)-C(6)	112.0			110.7		

[a] Distances in Å, angles in degrees; estimated average standard deviations of experimental values for (**2**) and (**3**), respectively: HH 0.004, 0.003, CC 0.002, 0.001, CH 0.003, 0.002 Å, HCH 0.2, 0.2, HCC 0.2, 0.1°.



(**2**)

Figure 1. Crystal structure of (**2**).



(**3**)

Figure 2. Crystal structure of (**3**).

Results of calculations with appropriately modified force fields will be reported in the full paper.

The observed shortening of the H(111) . . . H(121) distance of 0.041 Å on going from (**2**) to (**3**) is reproduced well by the calculations for (**1**) and (**4**). This indicates that (**4**) is a useful model for (**3**) as regards the present comparisons. According to the calculations the H . . . H shortening in (**3**) relative to (**2**) is a consequence of additional non-bonded repulsions between the sp^2 carbon atoms and the nearer hydrogen atoms of the ethylene bridges. A comparison of the observed and calculated bond angles at the congested methylene groups shows that our CFF performs somewhat better here than the MM2 force field, especially with respect to the above mentioned outward rocking deformations. The H–C–H angles at these methylene groups calculated with the CFF are about 1—2° larger than those observed, while those from MM2 are about 2—3° smaller (Table 1).

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