The CH···O Hydrogen Bond Adduct of two Trinitromethanes to Dioxane

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Recrystallization of $(O_2N)_3CH$ from dioxane yields the triple aggregate $(O_2N)_3CH\cdots O(CH_2CH_2)_2O\cdots HC(NO_2)_3$ with the shortest C(H)···O distances reported so far of 293.7(1) pm.

Studies aimed at isolation and structure determination of aci-nitromethane tautomers $[R_2C{=}N(O)OH]_n$[1] have included trinitromethane, cube-shaped crystals of which, (cubic space group Pa-3/205) with melting point 298.5 K, can be grown by 10 mbar sublimation at 281 K.[2,3] Attempts to crystallize from dioxane solution, however, yielded white needles, which after 10^{-2} mbar sublimation melted at 316.5 K and also can be obtained from $HCCl_3$ on *n*-pentane infusion.[2,4] Their structure analysis (Fig. 1) took us by surprise: instead of an expected polymorphic modification of $(O_2N)_3CH$, the CH···O bridged double adduct to dioxane was detected.†

In the crystal lattice (Fig. 1), the CH···O bonded triple molecule aggregates are aligned in strings with their polynitro ends $-C(NO_2)_3\cdots(O_2N)_3C-$ facing each other in a staggered arrangement. The strings from layers in the *yz* directions with alternating dioxane and trinitromethane units and the layers are stacked in the *x* direction so that the terraced aggregates fit optimally into each other. This spatially and, therefore, also energetically favourable packing motif is either due to or at least promoted by the CH···O hydrogen bond backbones, for which it provides a suitable framework.[5,6]

The dioxane molecule lies about a crystallographic inversion centre and the axes of the CH···O hydrogen bonds are consequently parallel. The distance C···O amounts to 293.7(1) pm and, after correcting the C–H bond length to 107 pm based on neutron diffraction results,[7,8] the H···O distance becomes 201 pm and the angle C–H···O 143°. According to a literature search[5–12] guided by the entries in the Cambridge Structural Database, it seems to be the shortest one of the known CH hydrogen bonds to an oxygen centre with a C···O distance below 300 pm. In two known terms of the van der Waals radii sum, $r_{\mathrm{OvdW}} + r_{\mathrm{CvdW}} < 150 + 175 < 325$ pm,[7,10] the distance would be contracted by about 30 pm or 9% due to the predominant coulombic attraction.[5–11] The relatively short

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† *Crystal data:* $M = 390.20$, triclinic, $P\bar{1}$, $a = 532.3(1)$, $b = 816.4(1)$, $c = 933.8(1)$ pm, $\alpha = 101.56(1)$, $\beta = 96.32(2)$, $\gamma = 98.95(1)°$, $V = 388.53 \times 10^6$ pm^3, $Z = 1$, $D_c = 1.668$ g cm^{-3}, Mo-Kα radiation, $\lambda = 71.073$ pm, $T = 200$ K. Of 2410 measured reflections ($3° < \theta < 60°$), 2284 were independent and 1534 with $I > 2\sigma(I)$. Four-circle diffractometer Siemens AED 2, direct methods (SHELXTL PLUS). C, N, O centres anisotropically refined, H with isotropic temperature factors. N_P 139, $R = 0.046$, $R_w = 0.049$, rest electron density $+0.38/-0.25$ e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

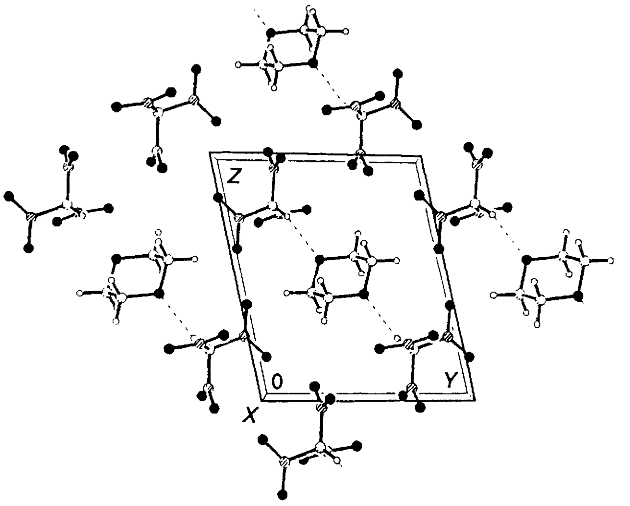

Fig. 1 Perspective view of crystal lattice packing and structure of the triple aggregate [$2(O_2N)_3CH{\cdot}O(CH_2CH_2)_2O$] [triclinic ($P\bar{1}$) unit cell with $Z = 1$; symbols ○: C/H, ◍: N, ●: O]. Selected average bond lengths (pm) and angles (°): C–N 149.7(3), N=O, 120.5(3), C–O(7) 143.3(2), C(H)···O 293.7(2); C–H···O(7) 146(2), N–C–N 109.0(2), C–N–O 116.0(2), O–N–O 127.5(2), C–O–C 109.9(1), O–C–C 110.6(2). The *cis* H–C–N–O torsion angles are in the range 35–49(1)°.

CH···O hydrogen bridges of the title aggregate further support the experimental correlation with pK_a values,[9,13] according to which their lengths decrease with increasing hydrocarbon acidity.[10,11] Within this context it has to be pointed out, however, that the structure of the trinitromethane molecule[3] does not change on formation of its dioxane adduct (Fig. 1) except for the torsional angles between the nitro groups, which partly decrease by about 10°. Because torsional distortions require only small amounts of energy,[14] they are, in general, easily compensated by either an increase in crystal lattice energy or especially by formation of even weak hydrogen bonds.

Energies of the usually rather weak CH···O hydrogen bonds are difficult either to measure or to retrieve from data correlations,[5,10] because they are usually masked by numerous other interactions. Recent highly correlated calculations[15] *e.g.* for methane hydrates $CH_4{\cdots}(OH_2)_n$ yield values between 2 and 4 kJ mol^{-1}. Nevertheless, for our bis(trinitromethane)–dioxane of about fivefold size, semiempirical PM3 calculations have been performed, which generally provide reliable results for hydrogen-bridged molecules.[16,17] They allow satisfactory reproduction of the crystallographic structure *via* geometry optimization (Fig. 1) including the CH···O distance of 293.7(1) pm. The only severe shortcoming, probably owing to insufficient parametrization of the electronically highly polarized polynitro molecules, is that the C–N bonds are predicted 7 pm too long. Based on the experimentally determined coordinates, a difference in the enthalpies of formation $\Delta\Delta H_{\mathrm{fPM3}} = -9$ kJ mol^{-1} result for the two hydrogen bonds, which is closer to the upper limit of the other estimates quoted,[5,10,14] and supported both by the rather high CH acidity of trinitromethane and the shortest C(H)···O hydrogen bond reported so far.

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