TABLE I

POTASSIUM SALTS OF TERMINAL DINITROMETHYL COMPOUNDS[a]

Potassium salt of	Yield, %	Potassium Calcd.	Potassium Found	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
1,1-Dinitropropane		22.70	22.92 22.62	20.92	21.12 20.85	2.93	3.18 3.10	16.28	16.23 16.17
1,1-Dinitropentane	70	19.53	19.65 19.83	30.00	30.06 30.25	4.53	4.40 4.66	14.00	14.15 14.18
4,4-Dinitrobutyric acid[b]	67	28.71	28.88 28.71	17.64	17.32 17.84	2.22	2.30 2.30	10.29	10.54 10.67

[a] See ref. 5 for spectral data. [b] Dipotassium salt, monohydrate.

fied to produce pure samples of the potassium dinitromethyl compounds for elemental analysis and for spectral determinations. Glover and Kamlet[2] have reported previously a method for preparing potassium salts of dinitromethyl compounds using potassium iodide. Where side reactions are possible (such as saponification), the iodide procedure is preferred.[3] For example, methyl 4,4,4-trinitrobutyrate readily gave the potassium salt of methyl 4,4-dinitrobutyrate with iodide, but with hydroperoxide a mixture of dipotassium 4,4-dinitrobutyrate and dipotassium 4,4-dinitrobutenoate was formed (see Table I for potassium salts of terminal dinitromethyl compounds).

Like iodide ion, hydroperoxide ion did not give 2,2-dinitroethanol from 2,2,2-trinitroethanol, but produced potassium nitroform, probably by deformylation.

Experimental[4]

Reduction Procedure.—To 0.01 mole of trinitromethyl compound in 25 ml. of methanol was added 5 ml. of 30% hydrogen peroxide. The solution was mixed and cooled in an ice bath to about 5–10°. Methanol (20 ml.) containing 4 g. of potassium hydroxide (0.07 mole) was cooled and added slowly with swirling. The solution became yellow immediately and a yellow solid began to precipitate. After all the potassium hydroxide was added, the solid was filtered cold with suction and washed with three 10-ml. portions of methanol.

The solid was then taken up in no more than 5 ml. of water and the mixture warmed gently to effect solution. If all of the peroxide was not washed out, this solution frothed until all the colorless gas was expelled. Two to three pellets of potassium hydroxide were then added and dissolved. Then methanol was added, if necessary, to cause precipitation to start. After about 5 min. the solid was filtered, washed with methanol, and dried at room temperature in a vacuum desiccator.

Attempted Preparation of Methyl Potassium 4,4-Dinitrobutyrate.—Methyl 4,4,4-trinitrobutyrate, 2.65 g. (0.0112 mole), was dissolved in 25 ml. of methanol in a 250-ml. erlenmeyer flask, and 5 ml. of 30% hydrogen peroxide was added at 25°. Potassium hydroxide, 2.2 g. (0.039 mole), in 10 ml. of methanol was added slowly with stirring. The solution became deep red and the temperature rose to 40–50°. The solution was cooled in an ice bath and a sticky solid precipitated. The liquid was decanted and methanol was added to the solid, which then became crystalline. The yellow-orange solid (I) was filtered and 2 g. of solid potassium hydroxide was added to the filtrate and dissolved, causing further precipitation. The solid which precipitated was filtered off and combined with the first batch (I) in methanol. The solid did not all dissolve when this mixture was warmed. After cooling the solution in an ice bath, the yellow-orange solid was filtered and dried in a vacuum desiccator. One gram of product was obtained.

The filtrate from the second batch of I, when evaporated by heating to one-fourth its volume (now 10 ml.), became quite red. The solution was cooled in an ice bath and a red solid (II) precipitated. The precipitate was filtered, and slurried with boiling methanol, and this mixture was cooled and filtered. While methanol-wet, the solid was quite red, but appeared to become yellowish when dry. After drying, the solid (II) weighed 0.15 g. The ultraviolet spectra showed λ_{max} water 381 mμ for I and 409 mμ[5] for II.

Anal. Calcd. for $C_4H_4K_2N_2O_6$ (I, dipotassium 4,4-dinitrobutyrate): K, 30.72. Found: K, 30.97.

Anal. Calcd. for $C_4H_2K_2N_2O_6$ (II, dipotassium 4,4-dinitrobutenoate): K, 30.98. Found: K, 29.43.

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[2] D. J. Glover and M. J. Kamlet, *J. Org. Chem.*, **26**, 4734 (1961).

[3] For the reaction of 1,1,1,3-tetranitropropane with hydroperoxide, see M. J. Kamlet, J. C. Dacons, and J. C. Hoffsommer, *ibid.*, **26**, 4881 (1961).

[4] *Caution:* As these compounds are explosive, they should be handled with appropriate precautions.

[5] M. J. Kamlet and D. J. Glover, *J. Org. Chem.*, **27**, 537 (1962), give 410 mμ (log ϵ 3.92) for this long wave-length peak.

The Twist-Boat Form of Cyclohexane

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In a number of recent discussions by organic chemists[2] of the twist-boat (C_2) form of cyclohexane, it has been stated or implied that the torsional or dihedral angles (ω_1 and ω_2 in I) of this molecule are 30 and 60°, a conclusion apparently arrived at by considering that these angles arise *halfway* through a pseudorotation cycle from one boat form to the next in which the relevant dihedral angles change from 0 to 60° and 60 to 60°, respectively. In fact, these angles are 33.2 and 70.6°; they may be computed from the equations given by Hazebroek and Osterhoff[3] in their earlier development of the flexible cyclohexanes (although these authors did not actually compute them) or more simply from the general equations for distances between points in space derived by the present author.[4]

These equations easily can be simplified for those cases with all bonds of equal length (d) and all bond angles tetrahedral (τ), the distances between atoms 1 and 4 (r_{14}) and between 1 and 5 (r_{15}), for example, being

$$r_{14}^2 = d^2(41-16 \cos \omega)/9$$

$$r_{15}^2 = 16d^2 [11-4 (\cos \omega_1 + \cos \omega_2) - \cos \omega_1 \cos \omega_2 + 3 \sin \omega_1 \sin \omega_2]/27$$

In the twist-boat form of cyclohexane (I), $l_1^2 = l_2^2 = 8/3$ (as a function of the intercepted tetrahedral angle) if the C–C bond length, d, is taken as unity. Since $l_1^2 = f_{15}(\omega_1,\omega_1)$, a solution of the second equation yields

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[1] Alfred P. Sloan Foundation Fellow.

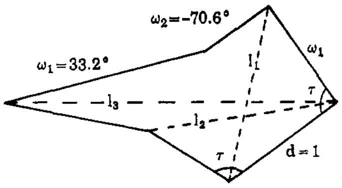
[2] *Cf.*, W. Klyne and V. Prelog, *Experientia*, **16**, 521 (1960); K. E. Howlett, *J. Chem. Soc.*, 4353 (1957); N. L. Allinger, *J. Am. Chem. Soc.*, **81**, 5727 (1959); R. D. Stolow, *ibid.*, **81**, 5806 (1959).

[3] P. Hazebroek and L. J. Osterhoff, *Discussions Faraday Soc.*, **10**, 87 (1951).

[4] J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961).

$$l_1^2 = 8/3 = 32/3 - [8(\cos \omega_1 + 1)/3]^2/3 \text{ and } \cos \omega_1 = 0.837 \ (\omega_1 = 33.2°)$$

Similarly, $l_2^2 = f_{15}\ (\omega_1,\omega_2)$, from which $\cos \omega_2 = 0.332$ ($\omega_2 = 70.6°$).



I

It is of value to point out this correction for two reasons, the first being that certain conformation conclusions can be very different. Thus, the axial length $l_3 = f_{14}(\omega_2) = 3.07$ Å. compared to 2.95 Å. for the chair (1,4-distance, $\omega = 60°$) or incorrect twist-boat ($\omega_2 = 60°$), so that calculations for quantities such as dipole moments could be seriously affected. Furthermore, a dihedral angle, ω_2, of 70.6° implies that *trans* fusion of a cyclopentane ring will be less strained than a *cis* fusion,[4] whereas if $\omega_2 = 60°$, there is no difference.

Secondly, it may be useful to emphasize that the dihedral angle changes in a given ring during pseudorotation are not simply linear. Table I illustrates the dihedral angle changes during pseudorotation of the boat forms of cyclohexane, discussed above, and the chair forms of cycloheptane (with tetrahedral bond angles),[4] for comparison.

TABLE I[a]

Cyclohexane			Cycloheptane		
Boat ⇌	twist-boat ⇌	boat	Chair ⇆	twist-chair ⇆	chair
60	33.2	0	62.0	55.1	62.0
0	33.2	60	−99.6	−79.8	−62.0
−60	−70.6	−60	81.7	103.2	99.6
60	33.2	0	0.0	−42.8	−81.7
0	33.2	60	−81.7	−42.8	0.0
−60	−70.6	−60	99.6	103.2	81.7
			−62.0	−79.8	−99.6

[a] All values in degrees.

Finally, it should be noted that dihedral angles of 30° and 60° do not form a ring. This can be shown by their substitution into the equation[4] for $r_{17} = f_{17}\ (\omega_1,\omega_2)$, which yields $r_{17} \neq 0$.