Acta Chemica Scandinavica B 28 (1974) 13—17

The Conformations of Some *gem*-Dimethyl Substituted Cyclic Anhydrides

GERD BORGEN

Kjemisk Institutt, Universitetet i Oslo, Oslo 3, Norway

Infrared spectroscopy shows that 3,3,6,6-tetramethyloctanedioic anhydride takes the same conformation in the crystal as in solution. Low-temperature ^{1}H NMR-spectroscopy of this 9-membered ring suggests C_2-symmetry, the two-fold axis passing through the ring oxygen in the anhydride group, and roughly D_3-symmetry for the ring skeleton. Two possible conformations are discussed for 3,3,7,7-tetramethylnonanedioic anhydride based on low-temperature NMR-spectroscopy, UV-absorptions, and dipole moment.

The acid anhydride group and two neighbouring carbon atoms should most likely tend to take the planar anti-anti form.[1] Also according to the determined crystal structure of monochloroacetic anhydride,[2a] electron diffraction of acetic anhydride [2b] and dipole moment investigations of benzoic and other anhydrides [3] the most stable conformation of the anhydride group seems to be the anti-anti form with varying deviations from planarity. In medium rings this conformation is not easily maintained and that is perhaps one of the reasons for the extreme instability of unsubstituted cyclic anhydrides.

We have earlier found that substitution with *gem*-dimethyl groups in certain positions facilitate the formation of 9- and 10-membered ring ketones.[4] Furthermore cyclic anhydrides of ring size 9 and 10, by substitution with *gem*-dimethyl groups were found to be easily formed and stable enough for conformational studies. In a previous paper [5] the syntheses of 3,3,6,6-tetramethyloctanedioic anhydride (a 9-membered ring), the corresponding dimer (an 18-membered ring), and 3,3,7,7-tetramethylnonanedioic anhydride (a 10-membered ring) have been described. A conformational analysis of these cyclic compounds is now reported.

In Table 1 the observed melting points, enthalpies and entropies of fusion and NMR coalescence temperatures at 100 MHz are listed. For comparison the anhydride of 3,3-dimethylpentanedioic acid (a 6-membered ring) has also been studied. (Pentane, octane, and nonanedioic anhydride = glutaric, suberic, and azelaic anhydride.)

In Table 2 the infrared absorption bands of the carbonyl groups, the ultraviolet absorp-

Table 1.

Compound	Ring-size	M.p. °C	Calorimetry ΔH_m	Calorimetry ΔS_m	NMR coalescense temp. at 100 MHc, °C
3,3,6,6-Tetramethyl-octanedioic anhydride	9	71	4.5	13.3	> 35
3,3,6,6-Tetramethyl-octanedioic anhydride dimer	18	liq.			
3,3,7,7-Tetramethyl-nonanedioic anhydride	10	59	4.9	14.9	*ca.* − 100
3,3-Dimethylpentane-dioic anhydride	6	123	4.3	11.9	> − 120

Table 2.

Compound	Infrared absorption cm^{-1}		Solvent	Ultraviolet absorption λ_{max}	ε	Solvent	Dipole moments [a] D
3,3,6,6-Tetramethyl-octanedioic anhydride							
Monomer	1758	1790	CCl_4	232	236	Hexane	4.1
Dimer	1735	1810	»				3.9
3,3,7,7-Tetramethyl-nonanedioic anhydride	1745	1790	»	230	215	»	3.7
3,3-Dimethylpentanedioic anhydride	1770	1815	»	223	< 100	»	5.0
Pentanedioic anhydride	1766	1811	CH_2Cl_2				4.14 [19]
Butanedioic anhydride	1797	1872	CCl_4	223	77	Ethyl ether	4.1
l-Methylbutanedioic anhydride				226	< 100	Heptane	
Acetic anhydride	1748	1824	None	217	56	None [18]	3.1 [3]
Propionic anhydride	1745	1810	»				3.3

[a] Solvent: Benzene.

tions and the dipole moments are shown, together with the corresponding values for some 5- and 6-membered ring anhydrides and the anhydrides of acetic and propionic acid.

No correlation was found between the splitting of the IR carbonyl bands and the conformation of the anhydride groups. Similarly the differences in the IR absorption intensities of the two carbonyl bands were not large enough to allow conclusions to be drawn concerning the angle between the two C=O bonds, as indicated by Fayat *et al.*[6] In the 6-membered cyclic anhydride the band at lowest frequency is the strongest, in the 9-membered ring the two bands are of the same intensity, in the 10- and 18-membered cyclic anhydrides the highest frequency bands are the strongest.

The shift of the UV-absorption of the carbonyl group is dependent on the resonance and inductive effect of the neighbouring groups. A positive resonance effect and a negative inductive effect will both shift the spectrum ($n-\pi^*$) towards shorter wavelengths.[7] The group

$$-O-\overset{\overset{O}{\|}}{C}-R$$

has a +R and −I effect. In our cyclic anhydrides the inductive effect is more or less the same for all possible conformations. The resonance effect through the free electron pairs of the "ether" oxygen and the electrons of the carbonyl group is dependent on the dihedral angle but this conjugation is possible both in the *cis-cis* conformations of rings and in the *trans-trans* conformation of acetic anhydride. This explains why the values for the 5- and 6-membered rings are almost the same as for acetic anhydride (Table 2). Conclusions about the conformations of the cyclic anhydrides are therefore difficult to draw from the UV absorption values.

3,3,6,6-TETRAMETHYLOCTANEDIOIC ANHYDRIDE

Studies of the conformations and barriers to inversion in 9-membered rings with *gem*-dimethyl groups in 4 and 7 positions have been reported earlier.[8,9] The compounds were all found to have C_2 symmetry, D_3 for the carbon skeleton, with the functional group and the *gem*-dimethyl substituted carbons on the three quasi symmetry axes of the D_3 ring skeleton.

The NMR-spectra of 3,3,6,6-tetramethyl-octanedioic anhydride in $CDCl_3$ at 35°, 20°, and 0° are shown in Fig. 1. There were no further changes in the spectrum below 0°. The coalescence temperature (above 35°C) is higher than found earlier for a correspondingly tetramethyl substituted cyclononanone.[8]

In the low temperature spectrum there are two lines for the *gem*-dimethyl protons, one for the methylenes between the *gem*-dimethyl

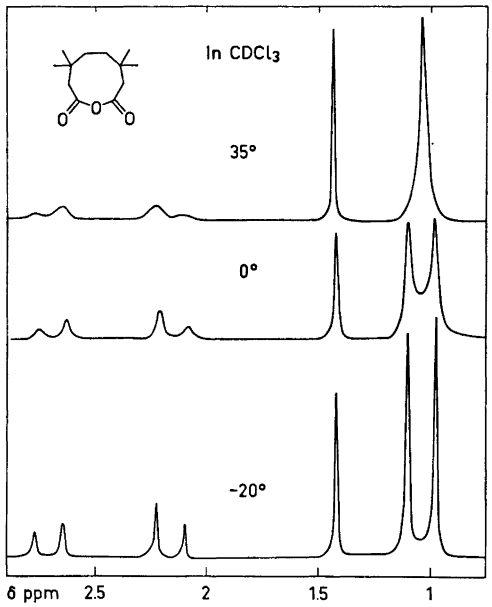

Fig. 1. The ^{1}H NMR-spectra of 3,3,6,6-tetramethyloctanedioic anhydride at different temperatures.

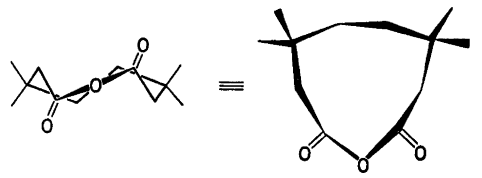

Fig. 2. Conformation of 3,3,6,6-tetramethyloctanedioic anhydride.

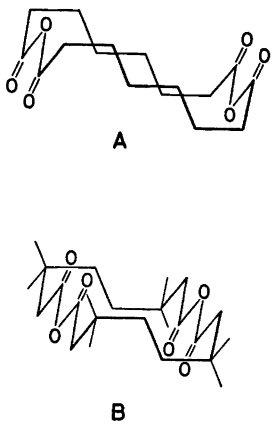

Fig. 3. A. Proposed ideal conformation for the unsubstituted dimer of octanedioic anhydride. B. Expected conformation for the dimer of 3,3,6,6-tetramethyloctanedioic anhydride.

groups and a quartet for the protons alpha to the anhydride groups. This means that there are only two types of methyl groups and two types of alpha protons. According to earlier considerations of possible conformations [8] this can only mean that the molecule has a C_2-symmetry, and probably D_3 symmetry for the ring skeleton, Fig. 2, as the earlier investigated tetramethyl substituted 9-membered rings.

The IR-spectra for the crystals and in CCl_4 solution were the same, indicating the same conformation in the crystals and in solution. The calorimetric values are in accordance with this observation.

DIMER OF 3,3,6,6-TETRAMETHYL-OCTANEDIOIC ANHYDRIDE

Hill and Carothers [10] found that the unsubstituted compound was stable up to the melting point 56 – 57°. Dale [1] has proposed that the ideal conformation for an unsubstituted cyclic dianhydride has the anhydride group and the two neighbouring carbon atoms coplanar to form the "bridges" as in Fig. 3 A; *gauche*-preferred bonds are in corner positions stabilizing the corners and the dipoles are anti-parallel.

In this conformation *gem*-dimethyl groups can, without serious interaction, only be placed in the corner positions, and not as they would in the tetramethyl substituted dimer, next to the corner positions.

Three other diamond lattice conformations are possible for the 18-membered cycloalkane.[11] Of these, the conformation, Fig. 3 B, would have planar anhydride groups, *gem*-dimethyl groups in the "corners", two-carbon bridges and dipoles opposed and would be the expected conformation for this compound, also because it most probably is the conformation for 1,1,4,4,10,10,-13,13-octamethylcyclo-octadecane.[12] However, the fact that the di-anhydride is a liquid and polymerizes by standing, may suggest that this conformation is not optimal, and makes it more probable that the dimeric anhydride exists as a mixture of conformations.

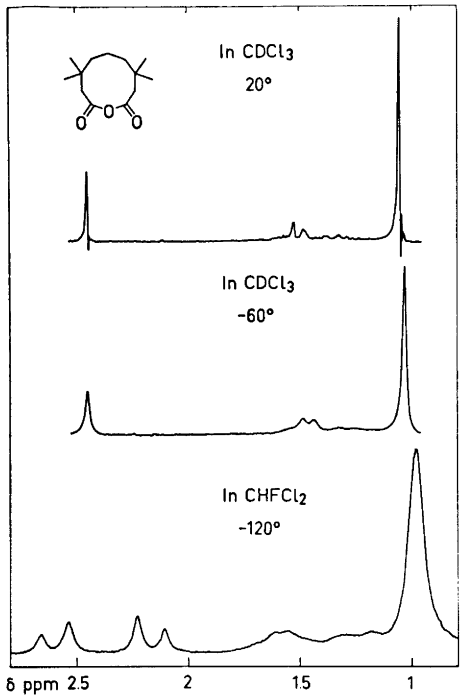

Fig. 4. The ^1H NMR-spectra of 3,3,7,7-tetramethylnonanedioic anhydride at different temperatures.

3,3,7,7-TETRAMETHYLNONANEDIOIC ANHYDRIDE

The NMR spectra of this 10-membered cyclic anhydride in $CDCl_3$ and $CHFCl_2$ at temperatures down to $-120°$ are shown in Fig. 4. The spectrum at the lowest temperature consists of a quartet for the alpha protons and the conclusion can be drawn that there are only two types of such protons and one type of α-CH_2 groups. The methyl signal has broadened but seems to require a lower temperature for full splitting. The spectrum at $-120°$ was the same in carbon disulphide. With only two types of alpha protons and the steric requirements of the two *gem*-dimethyl groups, the energetically possible conformations of this molecule are considerably reduced.

By semiquantitative calculations Dale [13] has found three probable conformations for 1,1,5,5-tetramethyl substituted cyclodecane. Two of these may be candidates for the conformation of the ring skeleton of 3,3,7,7-tetramethyl-

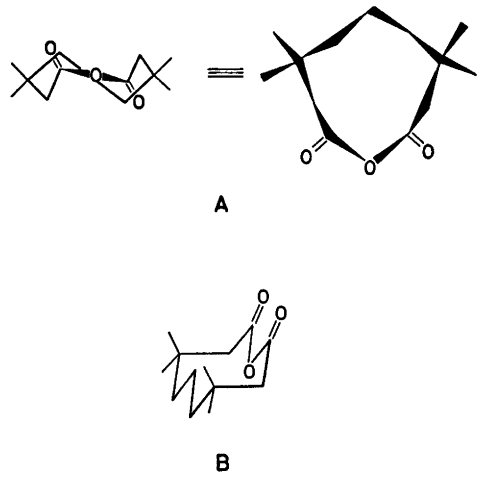

Fig. 5. Two possible conformations of 3,3,7,7-tetramethylnonanedioic anhydride.

nonanedioic anhydride. The third has no symmetry and is therefore not in accordance with the low temperature NMR-spectrum of the cyclic anhydride. The two actual conformations are shown in Fig. 5 A and B. Conformation A is the same as one of the two found by Dunitz in the crystal lattice of 4,4,8,8-tetramethylcyclodecane carboxylic acid.[14] Conformation B has already been proposed for cyclodecane-1,6-dione in solution.[15] The NMR-spectra, Fig. 4, shows a geminal coupling constant in the alpha protons of 12.5 cps. In conformation B one of the alpha protons is eclipsed with the C=O bond, in conformation A one alpha proton is almost eclipsed with the π-orbital in the C=O. In the first case the π-contribution to the coupling constant (dependent on the dihedral angle [16] should be below +0.5 cps, in the second case, −1.5 cps. As these contributions are small, and the observed coupling constant 12.5 cps is normal for such geminal protons (in the 9-membered ring anhydride, where the π-contribution should be zero, the corresponding J_{H-H}, was also 12.5) it is difficult to draw conclusions about the conformation from the geminal coupling constant of the alpha protons.

The similar degree of splitting of chemical shift of the two α-protons, as well as the similarity in the UV absorptions of the octane and nonane-dioic anhydrides indicates that the 10-membered cyclic anhydride may have the con-

formation A. The coplanarity in the anhydride group, preferred in open chain anhydrides may, however, be a reason for the molecule to chose conformation B. A surprising stability of this 10-membered cyclic anhydride, sligthly higher than the 9-membered ring anhydride is maybe explained by the coplanarity in conformation B and the stabilization of this conformation by the *gem*-dimethyl groups on the two "corners". As a cyclic anhydride the interactions are less and the deviations from the diamond lattice angles smaller than in the cycloalkane calculated by Dale and the conformation B therefore even more preferred.

The entropy and enthalpy of fusion of the tetramethylnonanedioic anhydride, Table 1, were on the same level as for the 9-membered ring anhydride. The IR-spectra were slightly different for the crystals in KBr and in CS_2 solution, however not sufficient to indicate different conformations in the two phases.

EXPERIMENTAL

Determination of dipole moments. Dielectric constants were measured at 20°C in a Weilheim Dipolmeter DM 01 in four different solutions of each compound. Refractive indices were measured on the same solutions in a Brice-Phoenix Differential Refractometer. Calculation of dipole moments was performed according to Hedestrand,[17] using no correction for atomic polarization.

Infrared spectra. These were recorded in a Perkin-Elmer Grating Infrared Spectrophotometer 457.

Ultraviolet spectra. The UV absorptions were determined in a Jasco Automatic Spectropolarimeter Model J-10.

Calorimetric measurements. A Perkin-Elmer Differential Scanning Calorimeter IB was used down to a temperature of −90°.

^1H NMR spectroscopy. The NMR spectra were recorded with a Varian HA 100 15 D instrument.

REFERENCES

1. Dale, J. *J. Chem. Soc.* (1963) 93.
2. a. De Kok, A. J. and Romers, C. *Rec. Trav. Chim. Pays-Bas 88* (1969) 625; b. Vledder, H. J., Mulhoff, R. C., Leyte, J. C. and Romers, C. *J. Mol. Struct. 7* (1971) 421.
3. Exner, O. and Jehlicka, V. *Collect. Czech. Chem. Commun. 35* (1970) 1514.
4. Borgen, G. and Dale, J. *Acta Chem. Scand. 26* (1972) 952.
5. Borgen, G. *Acta Chem. Scand. 27* (1973) 1840.
6. Fayat, C. and Foucaud, A. *Bull. Soc. Chim. Fr.* (1970) 4505.
7. West, W. *Chemical Applications of Spectroscopy, Technique of Organic Chemistry*, Interscience, New York/London 1956, Vol. IX, p. 661.
8. Borgen, G. and Dale, J. *Chem. Commun.* (1970) 1105.
9. Borgen, G., Dale, J. and Schaug, J. *Acta Chem. Scand. 26* (1972) 1073.
10. Hill, J. W. and Carothers, W. H. *J. Amer. Chem. Soc. 55* (1933) 5023.
11. Dale, J. *Pure Appl. Chem. 25* (1971) 469.
12. Borgen, G. and Dale, J. *Chem. Commun.* (1969) 447.
13. Dale, J. *Acta Chem. Scand. 27* (1973) 1149.
14. Dunitz, J. D. *Perspectives in Structural Chemistry*, Wiley, New York 1968, Vol. II, p. 21.
15. Alvik, T., Borgen, G. and Dale, J. *Acta Chem. Scand. 26* (1972) 1805.
16. Laszlo, P. and Stang, P. *Organic Spectroscopy*, Harpers and Row, New York 1971, p. 41.
17. Hedestrand, G. *Z. Phys. Chem. Abt. B 2* (1929) 428.
18. Suzuki, H. *Electronic Absorption Spectra*, New York 1967, p. 433.
19. Le Fèvre, R. J. W. and Sundaram, A. *J. Chem. Soc.* (1962) 4009.

Received August 27, 1973.