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THE STEREOCHEMICAL CONFIGURATION OF THE CYCLOÖCTATETRAENE DIHALIDES[1]

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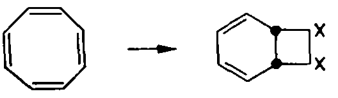
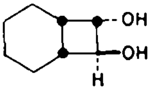
Abstract—The dichloride and the dibromide of cycloöctatetraene have the stereochemistry shown in formulae IIa and IIIa respectively. The reaction mechanisms leading to these configurations are discussed.

DIRECT chlorination or bromination of cycloöctatetraene (I) yields the dihalobicycloöctadienes II and III respectively,[2] and the gross structures of these products have been proved by synthetic, degradative,[3a,b] and spectral studies.[3c] The interesting stereochemical consequence of these reactions have already drawn attention,[3-6] and some stereochemistry has been established unequivocally.



I

II, X = Cl
III, X = Br



IV

The *cis* ring junctions in II, III and IV[3b,6] and the *trans* glycol configuration[3a,6] in IV (derived from II *via* a diacetate[2]) are known with certainty, but the assignment of the configurations of the halogen atoms in II and III stands on less firm ground. Either a *cis* or *trans* configuration of chlorine atoms in II could lead to the *trans* diacetate of IV if in the former case neighboring group participation by acetate[7] intervenes. Furthermore, acceptance of *trans* orientation of the halogen atoms in II and III based on *trans* addition to an unsaturated center[8,9] neglects, at least in the first approximation, complicating electronic participations that could obtain in the

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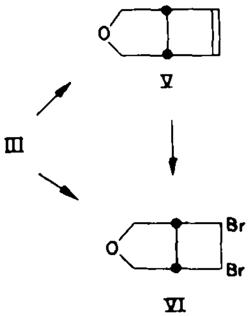
[1] Contribution No. 295, Department of Chemistry, Tufts University, Medford 55, Massachusetts.
[2] W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Liebigs Ann.* **560**, 1 (1948).
[3a] A. C. Cope and E. C. Herrick, *J. Amer. Chem. Soc.* **72**, 983 (1950).
[b] A. C. Cope and M. Burg, *ibid.* **74**, 168 (1952).
[c] E. R. Lippincott and R. C. Lord, *ibid.* **79**, 567 (1957).
[4] V. Georgian, *Chem & Ind.*, 1626 (1959).
[5] A. T. Blomquist and A. G. Cook, *Chem. & Ind.*, 873 (1960).
[6] E. Vogel, *Angew. Chem.* **65**, 346 (1953).
[7] S. Winstein, C. Hanson and E. Grunwald, *J.. Amer. Chem. Soc.* **70**, 812 (1948).
[8] I. Roberts and G. E. Kimball, *J. Amer. Chem. Soc.* **59**, 947 (1937).
[9] J. Hine, *Physical Organic Chemistry*, p. 214. (2nd Edition) McGraw-Hill, New York (1962).

unusual olefinic system of I ["tub" (D_{2d}) conformation (Ia)[10]] or in intermediates derived therefrom. A previous attempt at a partial solution to the problem of the relative halogen configurations in II and III using dipole moment measurements resulted in the proposal of a *cis* arrangement,[4] but this conclusion was challenged subsequently for the case of III.[5] In the latter investigation the proof offered for *trans* bromine atoms in III is not completely secure: compound V (prepared from III) was brominated to a dibromide VI which was identical with a dibromide obtained directly from III by a route not involving the halogenated carbon atoms. On the assumption that bromination of V occurs in the normal *trans* manner, the relative configurations of bromine atoms in VI and therefore in III will be *trans*. However, the validity of this assumption could be questioned on the premise that V might react with halogens atypically[11] because of the unusual geometry, strain, and the possibility of oxygen participation.



We now present evidence that establishes the complete stereochemical configurations of the cyclooctatetraene dihalides with certainty. The dichloride II has the stereochemistry shown in IIa (*cis* chlorine atoms) and the dibromide has the stereochemistry shown in IIIa (*trans* bromine atoms). These conclusions are based on the nuclear magnetic resonance (N.M.R.) spectra of the dihalocyclobutane-*cis*-1,2-dicarboxylic acids,[3,12] VII and IX prepared by permanganate oxidation of II and III respectively, and on the dipole moments[13] of the corresponding anhydrides VIII and X. Each anhydride could be quantitatively hydrolyzed to its diacid, indicating no

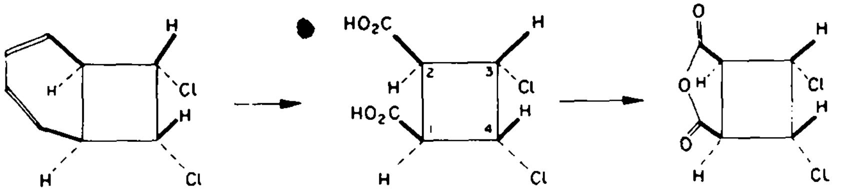
[10] W. B. Person, G. C. Pimentel, and K. S. Pitzer, *J. Amer. Chem. Soc.* **74**, 3437 (1952); F. S. Mathews and W. N. Lipscomb, *Ibid.* **80**, 4745 (1958); H. D. Springall, T. R. Whitey and R. C. Cass, *Trans. Farad. Soc.* **50**, 815 (1954); I. J. Lawrenson, and F. A. Rushworth, *Nature, Lond.* **182**, 391 (1958); O. Bastiansen, L. Hedberg and K. Hedberg, *J. Chem. Phys.* **27**, 1311 (1957).

[11] An increasing number of instances of *cis* chlorine and bromine additions to olefinic systems makes it hazardous to accept unquestioningly *trans* addition as the governing principle in all cases. Complicating stereoelectronic factors may loom importantly as departure is made from simple olefinic hydrocarbon cases. For cases of *cis* halogen additions see: T. Zincke, *Ber. Dtsch. Chem. Ges.* **10**, 999 (1877); S. Winstein and D. Seymour, *J. Amer. Chem. Soc.* **68**, 119 (1946); S. J. Cristol, F. R. Stermitz and P. S. Ramey, *Ibid.* **78**, 4939 (1956); J. A. Berson and R. Swidler, *Ibid.* **76**, 4060 (1954); H. Kwart and L. Kaplan, *Ibid.* **76**, 4078 (1954); W. G. Young, H. K. Hall, Jr., and S. Winstein, *Ibid.* **78**, 4338 (1956); R. K. Summerbell and H. E. Lunk, *Ibid* **79**, 4802 (1957); P. B. D. de la Mare and N. V. Klassen, *Chem. & Ind.* 498 (1960); R. K. Summerbell, personal communication, has observed substantial amounts of *cis* chlorine addition to dihydropyran in carbon tetrachloride in addition to the *trans* product.

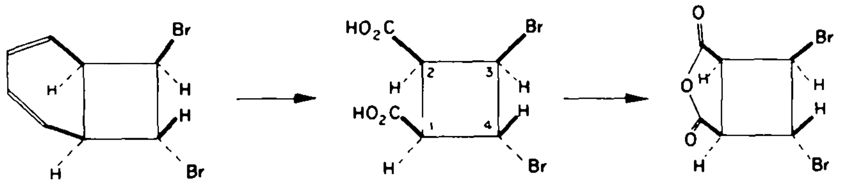
[12] E. Vogel, *Liebigs Ann.* **615**, 14 (1958).

[13] We are grateful to Prof. Max T. Rogers for the dipole moment measurements.

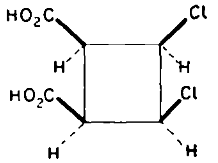
change in halogen configuration during anhydride formation (reagent, acetyl chloride), and confirming the *cis* arrangement of carboxyl groups in VII and IX.



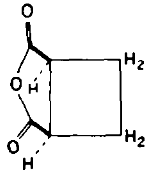
IIa VII VIII



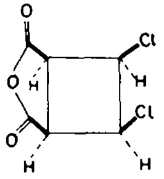
IIIa IX X



XI



XII



XIII

The N.M.R. spectra of the two dihalodiacids are strikingly different and the general appearance of absorption for protons attached to carbon is shown in Fig. 1. The spectrum of the dichloro compound VII contains one multiplet centered at δ 5·46 p.p.m. for H-3 and H-4, and another multiplet centered at δ 4·18 p.p.m. for H-1 and H-2. This is a typical A_2X_2 pattern, the multiplets being symmetrical about the midpoint between them and each multiplet being symmetrical about its own midpoint. Proton H-1 is therefore chemically equivalent to H-2, and H-3 to H-4. It is only possible to have two pairs of chemically equivalent protons when there is a plane of symmetry in the molecule. This requirement is met only if the chlorine atoms are *cis* to each other and therefore *trans* chlorine atoms are clearly excluded. Two possibilities remain: structures VII and XI in which the chlorine atoms are *trans* and *cis* respectively to the carboxyl groups. It was hoped to distinguish between these by the relationship between coupling constant and dihedral angle (Karplus equation). However, analysis for the coupling constants shows that the usual form of the Karplus equation cannot be applied in these cyclobutane derivatives and no stereochemical deductions could be based on it. The analysis of the splitting patterns is nevertheless interesting and is presented below as an Addendum.

Dipole moment measurements on the anhydride of the dichlorodiacid permit a clear decision between structures VII and XI. The value obtained in benzene solution at 25° was 1·96D and that for the parent cyclobutane dicarboxylic anhydride XII[14] was 4·28D. The latter value is concordant with moments of 4·2D and 4·3D for succinic and citraconic anhydrides[15] respectively, indicating no unusual effects from fusion of the anhydride to the cyclobutane ring. The fact that the moment of the dichloroanhydride is much less than that of the parent compound XII proves that the moment of the *cis* chlorine atoms is directed nearly antiparallel to the moment of the anhydride group, and the magnitude of the difference, 2·3D, is consistent with the dipole moment of 2·5D found previously[4] for the *cis* dichloride II. Thus the dichloroanhydride must have the stereochemistry shown in structure VIII. The other anhydride having *cis* chlorine atoms (XIII) is clearly excluded because the presence of all the electron attracting groups on the same side of the cyclobutane ring would result in a dipole moment of 5–6D. Therefore the dichlorodiacid is VII and cycloöctatetraene dichloride is IIa.

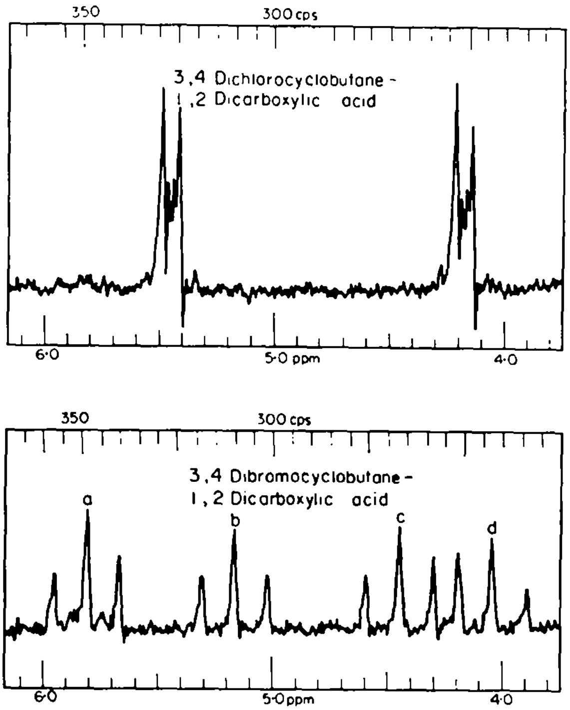


FIG. 1. N.M.R. spectra at 60 Mcps for the dihalodiacids VII and IX in pyridine solution. The scales refer to internal tetramethylsilane at zero.

The N.M.R. spectrum of the dibromodiacid IX exhibits four triplets (labelled *a*, *b*, *c*, *d*), each for one proton, at δ 5·79, 5·16, 4·45 and 4·04 p.p.m. Triplets *a* and *b* are assigned to H-3 and H-4 (not necessarily respectively) and triplets *c* and *d* to H-1 and H-2. The marked differences in chemical shift demand that each ring proton be in a different electronic and geometric environment, that is, there are no chemically

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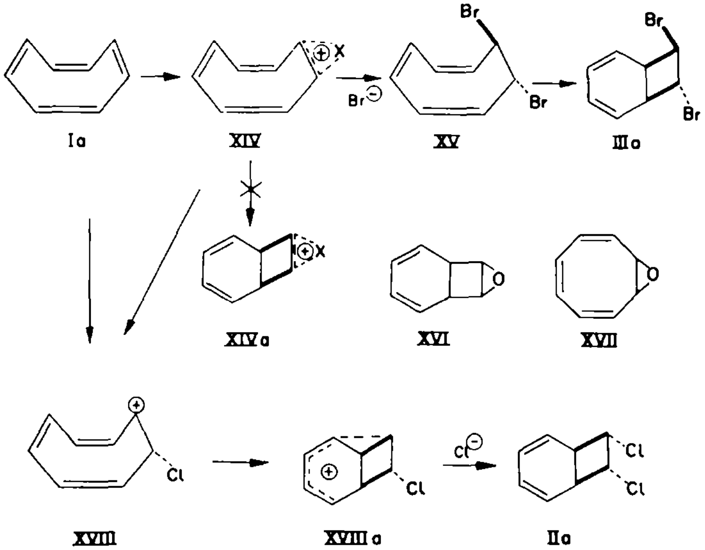
[14] W. H. Perkins, Jr. *J. Chem. Soc.* **65**, 572 (1894); E. R. Buchman, A. O. Reims, T. Skei and M. Schlatter, *J. Amer. Chem. Soc.* **64**, 2696 (1942).

[15] M. A. G. Rau and N. Anantanarayanan, *Proc. Indian Acad. Sci.* **5A**, 185 (1937).

equivalent pairs of protons in the dibromide. This condition is satisfied only if the bromine atoms are *trans* to each other, and only one structure is then possible, the racemate IX. Again the analysis of the splitting patterns (see Addendum) does not yield useful stereochemical information. The dipole moment of the dibromoanhydride X was 2·50D. This compares with a value of 3·0–3·5D calculated on the basis of certain assumptions which have been listed previously[4] about the planarity of the ring and the magnitude of the various bond angles. We believe the discrepancy between the observed and the expected moment does not render structure X in doubt, but instead it reflects the degree of uncertainty in the dipole calculations. For example, the cyclobutane ring probably is neither exactly square nor planar. The relative stereochemistry of cycloöctatetraene dibromide is therefore as depicted in IIIa.

A mechanism which would account reasonably for the generation of the dihalides may be represented as follows. Electrophilic attack by halogen on Ia[10] may produce the halonium ion XIV (the experimental facts in the generation of II and III are quite



clearly in conformity with an ionic mechanism-low temperature, immediate consumption of halogen, radical initiators such as light not necessary, good yields of single products). Ion XIV may be expected to be sufficiently important in the case of the bromonium intermediate (XIV, X = Br) to lead to the *trans* dibromide XV by the usual bromide displacement process. The bicyclic form IIIa would be expected to follow by a valency tautomerism established for cycloöctatriene by Cope.[16] The question of whether in fact ion XIV collapses to the bicyclic form XIVa before attack by bromide ion can probably be settled in the negative by considering the case of cycloöctatetraene oxide. If ion XIVa (X = OH) were the intermediate in the peracid conversion of cycloöctatetraene to its oxide, then loss of a proton would produce structure XVI. Whereas the oxide had been thought to possess the tricyclic form

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[16] A. C. Cope, A. C. Haven, Jr., F. L. Ramp and E. R. Trumbull, *J. Amer. Chem. Soc.* **74**, 4867 (1952). For an excellent discussion in the general area of valency isomerism of the type discussed here, see E. Vogel, O. Roos and K-H. Disch, *Liebigs Ann.* **653**, 55 (1962).

XVI,[2] the octatrienic structure XVII was later established as the correct one.[17] Since XVI and XVII are valence isomers, the steric strain inherent in a tricyclic form such as XVI, and thus XIVa, apparently rules out any significant intercession of a tricyclic ion, and the bicyclic is favored. This proposal has subtance only if the cyclic halonium ion is sufficiently stable, which is quite reasonable in the case of bromonium,[18] XIV (X = Br).

The situation is then changed when chlorine is involved, as the cyclic chloronium[19] ion may not be expected to compete favorably with an alternative chlorocarbonium species.[18,20] Whether in fact a form XIV (X = Cl) intervenes at all on electrophilic attack by chlorine may be questioned, but the most reasonable event subsequent to such an attack would be the immediate generation of the chlorocarbonium ion XVIII. Because of the non-planarity in XVIII there would not be opportunity for adequate orbital overlap between the adjacent unsaturated centers and the vacant p orbital at the cationic carbon atom. There would be, therefore, considerable driving force to form the valence tautomeric[16] ion XVIIIa, where there is present the opportunity for overlap with the p orbitals of the cyclohexadiene system. The alternative of flattening the octatrienic ring of XVIII to permit orbital overlap is sterically ruled out on the basis of a host of evidence which indicates little or no interaction between adjacent unsaturated centers in the eight membered ring. This example of neighboring group participation is analogous to the large number of cases studied by Winstein involving anchimeric effects of π-electronic systems.[21,22] The steric consequence of chloride ion attack on XVIIIa would be the observed *cis* dichloride IIa.[23]

The stereochemical variations in the products IIa and IIIa which attend the change in the halogen used are noteworthy and relevant to other cases of a similar effect.[24] Whereas electrophilic addition of bromine to olefins seems to be consistently *trans*[25]

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[17] A. C. Cope, P. T. Moore and W. R. Moore, *J. Amer. Chem. Soc.* **80**, 5505 (1958).

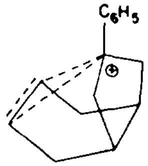
[18] S. Winstein, E. Grunwald, and L. I. Ingraham, *J. Amer. Chem. Soc.* **70**, 821 (1948).

[19] H. J. Lucas, and C. W. Gould, Jr., *J. Amer. Chem. Soc.* **63**, 2541 (1941).

[20] P. B. D. de la Mare and N. V. Klassen, *Chem. & Ind.* 498 (1960).

[21] A few refs. only need be cited: S. Winstein and R. Adams, *J. Amer. Chem. Soc.* **70**, 838 (1948); M. Simonetta and S. Winstein, *Ibid.*, **76**, 18 (1954); S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *Ibid.*, **77**, 4183 (1955).

[22] An interesting and somewhat related case involving stabilization of a cationic center by overlap with a geometrically favorably oriented π-orbital system is that of the stable non-classical bicyclic ion:



G. Leal and R. Petit, *J. Amer. Chem. Soc.* **81**, 3160 (1959).

[23] A modification of the mechanism proposed above leading to *cis* chlorine configuration would involve including in the description of the chlorocationic species (XVIII, XVIIIa) the concept of the ion pair with chloride ion, either free (W. G. Young, H. K. Hall, Jr., and S. Winstein, *J. Amer. Chem. Soc.* **78**, 4338 (1956) or incipiently produced from a σ-complex with chlorine (ref. 20).

[24] For a change in stereochemical result in going from bromonium to chloronium ion, see S. Winstein and D. Seymour, *J. Amer. Chem. Soc.* **68**, 121 (1946).

[25] The only exception we know of is that reported by both Berson and Kwart (ref. 11) in which case the intercession of a radical mechanism is suspected.

addition of chlorine engenders much *cis* product in any instance where a better cationic species may compete with the postulated cyclic chloronium ion. Usually *cis-trans* mixtures have resulted[11] but the particularly favorable geometry of the ion XVIIIa has led in the case of cycloöctatetraene to what is probably the most stereoselective *cis* addition of chlorine to an olefin.

Since the cycloöctatetraene dihalides have been used as intermediates in other interesting transformations,[26] their different stereochemistry may prove to be important in a detailed accounting of these changes.

ADDENDUM

Analysis of splitting in the N.M.R. *spectra*

with L. F. JOHNSON, Varian, Associates, Palo Alto

1. 3,4-*Dichlorocyclobutane*-1,2-*dicarboxylic acid* (VII)

The spectrum of the dichlorodiacid reproduced in Fig. 1 does not show all of the fine structure in each multiplet because of the noise level. Spectra taken at higher concentration and gain reveal additional tiny satellites; the full splitting pattern for the high field two proton multiplet is shown in Fig. 2. The low field multiplet is identical. Spectra run at 60 Mcps and 100 Mcps confirm that the eight lines in each multiplet are real and due to splitting. Analysis of the A_2X_2 pattern for the coupling

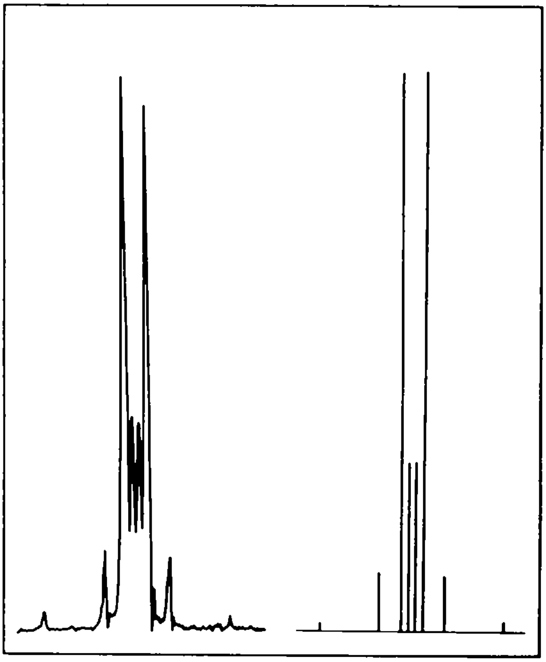


FIG. 2. Experimental (high gain) and calculated splitting patterns for the higher field multiplet in the NMR spectrum of the dichlorodiacid VII.

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[26] e.g., R. Criegee, W. Horäuf and W. D. Schellenberg, *Chem. Ber.* 86, 126 (1953).

constants was carried out according to Pople *et al.*[27] using the following measured values of the line positions from the center of gravity (figs in brackets are the transition numbers in the notation of Pople *et al.*): +17·8 c.p.s. (5); +6·0 (10); +2·2 (1, 2, 9 overlapping); +0·65 (6); −0·65 (7); −2·2 (3, 4, 12 overlapping); −6·0 (11); −17·8 (8). The coupling constants thus derived are: $J_{A,A'} = 6{\cdot}3$ c.p.s.; $J_{X,X'} = 10{\cdot}6$ c.p.s.; $J_{A,X} = J_{A',X'} = 5{\cdot}9$ c.p.s.; $J_{A,X'} = J_{A',X} = -1{\cdot}5$ c.p.s. Calculation of the theoretical spectrum using these coupling constants gives the pattern shown in Fig. 2, in excellent agreement with the observed multiplet. $J_{A,A'}$ and $J_{X,X'}$ must represent $J_{1,2}$ and $J_{3,4}$ in VII although it is not possible to tell which is which. Nevertheless both $J_{1,2}$ and $J_{3,4}$ (6·3 and 10·6 c.p.s.) are coupling constants between vicinal *cis* protons and the difference in magnitude between them is interesting. Similarly, J_{AX} and $J_{AX'}$ represent $J_{1,4}$ (equals $J_{2,3}$) and $J_{1,3}$ (equals $J_{2,4}$). It seems reasonable to assume that the larger of these coupling constants (5·9 c.p.s.) is $J_{1,4}$ between vicinal *trans* hydrogens and the smaller (−1·5 c.p.s.) is $J_{1,3}$ for the long range coupling between the *trans* protons diagonally across the ring. The difference between $J_{AA'}$ and $J_{XX'}$ (both for vicinal *cis* protons) and the similarity between $J_{AA'}$ and J_{AX} (the latter for vicinal *trans* protons) presumably implies considerable puckering or strain in the ring. It is also clear that the stereochemistry of VII could not have been inferred from the coupling constants.

2. 3,4-*Dibromocyclobutane*-1,2-*dicarboxylic acid* (IX)

The general appearance of the four discrete triplets (*a*, *b*, *c*, *d*) in the N.M.R. spectrum at 60 Mcps in Fig. 1 remains unchanged in spectra run at 100 Mc.p.s. On grounds of relative chemical shift, triplets *a* and *b* at lower field are ascribed to protons on carbon carrying bromine atoms, and triplets *c* and *d* at higher field to the protons α to the carboxyl groups. Thus protons *a* and *b* are vicinal, as are protons *c* and *d*. An expanded trace of a vacuum degassed solution reveals additional fine structure in that each branch of triplets *b* and *d* is split by 0·5 c.p.s. The small coupling means that the *b* and *d* protons are diagonally opposite each other and thus proton *c* is adjacent to *b* on the other side from *a*. This assignment permits the following coupling constants to be measured directly from the expanded trace: $J_{a,b} = 8{\cdot}7$ c.p.s.; $J_{a,d} = 8{\cdot}7$ c.p.s.; $J_{b,c} = 8{\cdot}7$ c.p.s.; $J_{c,d} = 9{\cdot}2$ c.p.s.; $J_{b,d} = 0{\cdot}5$ c.p.s.; $J_{a,c} = 0{\cdot}0$ c.p.s. Decoupling experiments[28] at 100 Mc.p.s. confirm these relative spin-spin couplings. When triplet *d* was irradiated using a difference frequency of 175 c.p.s. (corresponding to $\delta_d - \delta_a$ at 100 Mc.p.s.), triplet *a* collapsed to a doublet ($J_{a,b}$ remains), thus proving that *a* is indeed strongly coupled to *d*, not *c*. Similarly, irradiation of triplet *c* using a difference frequency of 70 c.p.s. (corresponding to $\delta_c - \delta_b$) caused *b* to collapse to a doublet ($J_{a,b}$ remains). On the present evidence there is no unquivocal way of assigning the protons as in IXa (in which H-3 corresponds to triplet *a*, etc.) or as in IXb (in which H-4 corresponds to triplet *a*, etc.). Nor is it possible to tell if the long range coupling $J_{b,d}$ is of equal or opposite sign to that of the four vicinal coupling constants. Clearly $J_{a,b}$ and $J_{c,d}$ are coupling constants between vicinal *trans* and *cis*

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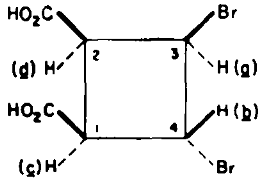
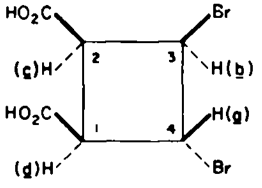
[27] J. A. Pople, W. G. Schneider and H. J. Bernstein, *High Resolution Nuclear Magnetic Resonance* p. 141. McGraw-Hill, New York (1960).

[28] The decoupling method used is that described by R. Freeman and D. H. Whiffen, *Mol. Phys.* **4**, 321 (1961). The instrumentation is described in Varian Associates' *Technical Information Bulletin* Vol. 3, No. 3 (1961).



IXa



IXb

pairs of protons respectively. If $J_{a,d}$ is a vicinal *cis* coupling then $J_{b,c}$ is a vicinal *trans* coupling (IXa) or vice versa (IXb). In either case the four main couplings $J_{a,b}$, $J_{a,d}$, $J_{b,c}$ and $J_{c,d}$ represent two vicinal *cis* and two vicinal *trans* couplings, yet they all have practically the same magnitude. As before, the coupling constants could not have been used to make stereochemical deductions.

EXPERIMENTAL

cis-*Cyclobutane*-1,2-*dicarboxylic acid anhydride*. This substance was prepared essentially according to the method of Buchman *et al.*[14,29] The mixture of liquid and solid isomers of diethyl α,α′-dibromoadipate,[30] b.p. 165–169: (7–8 mm),[31] was converted (potassium cyanide in methanol) to dimethyl 1-cyano-1,2-cyclobutane dicarboxylate, b.p. 120–123: (0.8 mm) which was then hydrolyzed (refluxing 6N hydrochloric acid) to a crude cyclobutane tricarboxylic acid. The latter was thermally (170–180° (20 mm), 3 hr) decarboxylated and converted to the anhydride of *cis*-cyclobutane-1,2-dicarboxylic acid by means of acetyl chloride and recrystallized several times from dry benzene, m.p. 77–78°.

3,4-*Dichlorocyclobutane*-1,2-*dicarboxylic acid anhydride* (VIII). 3,4-Dichlorocyclobutane-1,2-dicarboxylic acid, prepared according to Cope and Burg,[3b] m.p. 182–183°.[32] (Found: C, 33·82; H, 2·73. $C_6H_6O_4Cl_2$ requires: C, 33·83; H, 2·84%), was taken up in ten volumes acetyl chloride (reagent grade) and refluxed 3 hr. Removal of volatile matter yielded a crystalline residue which was recrystallized twice from sodium dried benzene, m.p. 182–183·4°. (Found: C, 36·70; H, 1·75. $C_6H_4O_3Cl_2$ requires: C, 36·95; H, 2·05%).

A sample of this anhydride (VIII) dissolved in acetone was treated with a few ml water, allowed to stand 1 hr, and evaporated to dryness in a rotary evaporator with minimum heat. There resulted a practically quantitative conversion to the diacid VII, m.p. 181–183°, undepressed on admixture with authentic diacid, but depressed by the anhydride. I.R. comparisons of diacid as originally prepared and that regenerated from the anhydride established further complete identity.

3,4-*Dibromocyclobutane*-1,2-*dicarboxylic acid anhydride* (X). Cycloöctatetraene dibromide[2] was oxidized (potassium permanganate) to the dibromocyclobutanedicarboxylic acid IX, m.p. 191–192°, by the method of Vogel.[33] The acid IX was converted to the anhydride X by means of acetyl chloride as described above for the case of VIII. The anhydride X was recrystallized twice from dry benzene-hexane, m.p. 156·5–157·5°. (Found: C, 25·62; H, 1·43; Br, 56·46. $C_6H_4O_3Br_2$ requires: C, 25·45; H, 1·41; Br, 56·30%).

A sample of the anhydride X in acetone-water was reconverted to the original acid IX, nearly quantitatively, as discerned by m.p. and I.R. comparisons.

N.M.R. spectra were taken on Varian Associates A-60 and HR-100 instruments. Pyridine was used as solvent for the dihalodiacids and tetramethylsilane as internal reference.

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[29] See also N. L. Allinger, M. Nakazaki and V. Zalkow, *J. Amer. Chem. Soc.* **81**, 4074 (1959).

[30] P. C. Guha and D. K. Sankaran, *Organic Syntheses*, Coll. Vol. III, p. 623. John Wiley, New York, N.Y. (1955).

[31] A lower b.p. 122° (7 mm) was reported in ref. 29.

[32] A somewhat lower m.p. 176·8–178° was reported in ref. 3*b*.

[33] E. Vogel, *Leibigs Ann.* **615**, 14 (1958).