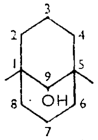
218. *Bridged Ring Systems. Part V.* Structural Assignments in the Bicyclo*[3,3,1]*nonane System by Infrared Spectroscopy.*

By G. EGLINTON, J. MARTIN, and W. PARKER.

High resolution infrared spectroscopy has permitted a determination of the configurations of the epimeric 1,5-dimethylbicyclo[3,3,1]non-2-en-9-ols. The occurrence of hydrogen bonding (OH→π) in one isomer has been related to gas–liquid chromatographic retention times of these compounds. The appearance of ν(CH) and δ(CH_2) absorptions at abnormally high frequencies can be correlated with the non-bonded intractions inherent in this ring system, and strongly indicate the unexpected twin-chair conformation for the bicyclo[3,3,1]nonane framework.

IN view of the semi-rigid nature of the bicyclo[3,3,1]nonane ring system, an examination of the chemical and physical properties of a series of such compounds was of interest.[1] In the present work a detailed survey of the infrared spectra has revealed unusual absorptions



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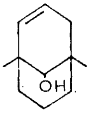

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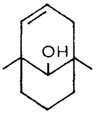

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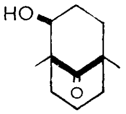

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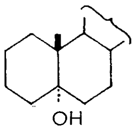

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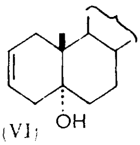

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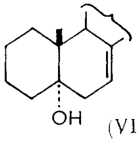

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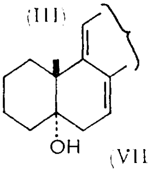

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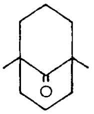

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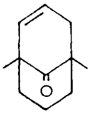

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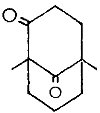

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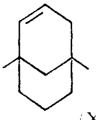
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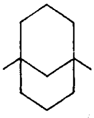
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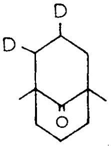

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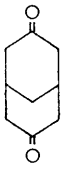

(XV)

TABLE 1.

Hydroxyl stretching absorptions in carbon tetrachloride.

No.	Compound	ν (O–H)	$\Delta\nu_{\frac{1}{2}}$[a]	ε[a]
(I)	1,5-Dimethylbicyclo[3,3,1]nonan-9-ol	3643	15	60
		3625sh	(17)	(10)
(II)	*anti*-1,5-Dimethylbicyclo[3,3,1]non-2-en-9-ol	3640	15	70
		3625sh	(19)	(10)
(III)	*syn*-1,5-Dimethylbicyclo[3,3,1]non-2-en-9-ol	3640	23	15
		3584	18	50
(IV)	2-Hydroxy-1,5-dimethylbicyclo[3,3,1]nonan-9-one	3630	20	70
(V)	Cholestan-5α-ol	3631	(17)	30
		3613	(16)	30
(VI)	Cholest-2-en-5α-ol	3613	21	25
		3596	18	45
(VII)	Ergost-7-en-5α-ol...	3614sh	(25)	(10)
		3593	29	40
(VIII)	Ergosta-7,9,22-trien-5α-ol	3583	20	—

Concentrations: 0·001—0·002M, 2 cm. cell except for compounds (I) 0·05M, 0·51 mm. cell, and (VIII) saturated solution, 2 cm. cell. Absorptions were concentration-independent at these dilutions. sh, Shoulders: extinction coefficients and half band widths were estimated by allowing for absorption of main band, *i.e.*, by graphical separation (cf. ref. 3). Values in parentheses are approximate.

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* Part IV, Buchanan, McKillop, and Raphael, *J.*, 1965, 833.

[1] Part III, Martin, Parker, and Raphael, *J.*, 1964, 289.

which can be related to the stereochemistry and conformation of this system. The compounds studied were the bicyclo[3,3,1]nonane derivatives (I—IV), and (IX—XV) and related reference compounds (V—VIII). The infrared data are listed in Tables 1—5 and illustrated in Figs. 1—4.

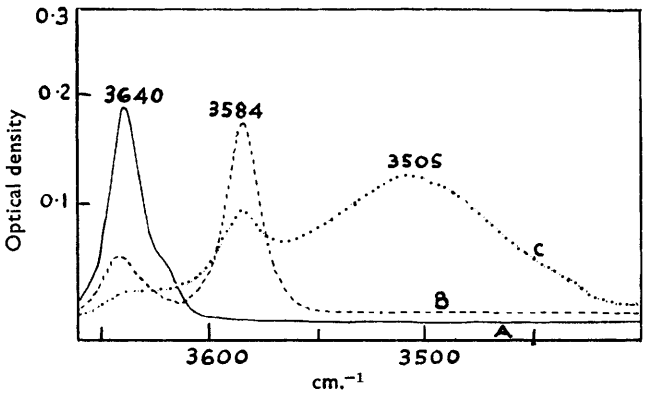


FIG. 1. Hydroxyl stretching absorptions of *anti*- and *syn*-1,5-dimethylbicyclo[3,3,1]non-2-en-9-ol (II and III). (*A*), Compound (II) in carbon tetrachloride (0·0013M; 2 cm. cell); (*B*), compound (III) in carbon tetrachloride (0·0016M; 2 cm. cell); and (*C*), compound (III) in 1 : 1 ether–carbon tetrachloride (0·0085M; 2 mm. cell).

TABLE 2.

Olefinic absorptions.*

No.	Compound	ν(CH)	$\Delta\nu_{\frac{1}{2}}{}^{a}$	ε^{a}	ν(C=C)	$\Delta\nu_{\frac{1}{2}}{}^{a}$	ε^{a}	γ(CH)	$\Delta\nu_{\frac{1}{2}}{}^{a}$	ε^{a}
(XII)	1,5-Dimethylbicyclo-[3,3,1]non-2-ene	3014	17	65	1670	(15)	(5)	710	5	175
					1640	(15)	(10)			
(II)	*anti*-1,5-Dimethyl-bicyclo[3,3,1]non-2-en-o-ol	3012	16	70	1672	15	10	711	5	240
					1653	6	20			
(III)	*syn*-1,5-Dimethylbicyclo[3,3,1]non-2-en-9-ol [b]	3017	17	65	1681 [b]	(15)	5	716 [b]	10	130
					1643 [b]	(15)	10			
(X)	1,5-Dimethylbicyclo-[3,3,1]non-2-en-9-one	3019	15	60	1660	—	—	719	7	80
					1652 [c]	(10)	(20)	696	6	165

* ν(CH) and ν(C=C) absorptions measured in carbon tetrachloride (concentration: 0·05—0·1M 0·51 mm. cell), and γ(CH) absorptions measured in carbon disulphide (0·025—0·071M, 0·5 mm. cell). Refs. as in Table 5.

TABLE 3.

Carbonyl stretching absorptions in carbon tetrachloride.*

No.	Compound	ν(C=O)	$\Delta\nu_{\frac{1}{2}}{}^{a}$	ε^{a}
(IX)	1,5-Dimethylbicyclo[3,3,1]nonan-9-one	1714	9	700 [d]
(X)	1,5-Dimethylbicyclo[3,3,1]non-2-en-9-one	1720	8	700 [d]
(IV)	2-Hydroxy-1,5-dimethylbicyclo[3,3,1]nonan-9-one	1716	12	510
(XI)	1,5-Dimethylbicyclo[3,3,1]nonane-2-9-dione	1737	10	230
		1707 [b]	13	730
(XV)	Bicyclo[3,3,1]nonane-3,7-dione	1729 [b]	15	845

* Concentrations: 0·02—0·04M in 0·51 mm. cells.
Refs. as in Tabie 5.

TABLE 4.

Solvent dependence of the carbonyl stretching absorptions * of 1,5-dimethylbicyclo[3,3,1]nonane-2,9-dione (XI).

Solvent	ν^{1}(C=O)	$\Delta\nu_{\frac{1}{2}}{}^{a}$	ε^{a}	ν^{2}(C=O)	$\Delta\nu_{\frac{1}{2}}{}^{a}$	ε^{a}	$\Delta\nu = (\nu^{1} - \nu^{2})$
Hexane	1741	(15)	245	1712 [b]	13	735	29
Carbon tetrachloride	1737 [b]	(20)	230	1707 [b]	13	730 [d]	30
Chloroform	1729	(20)	255	1701 [b]	17	725	28
Acetonitrile	1728	(20)	250	1702 [b]	17	640	26

* Concentrations: *ca.* 0·01M in 0·51 mm. cells except for carbon tetrachloride (0·0014M, 5 mm. cell).
Refs. as in Table 5.

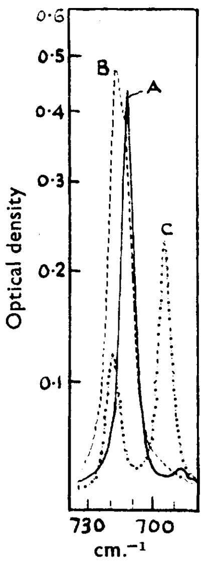


FIG. 2.

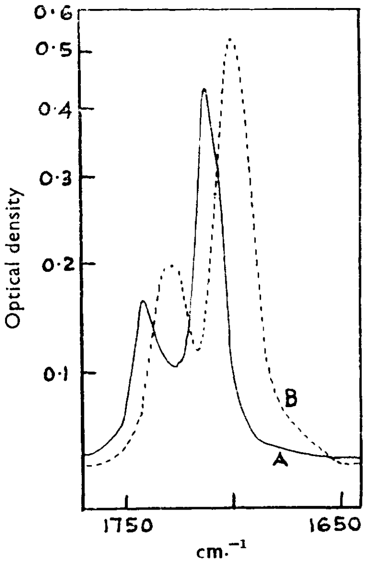


FIG. 3.

FIG. 2. Olefinic C–H out-of-plane deformations of *anti*- and *syn*-1,5-dimethylbicyclo[3,3,1]non-2-en-9-ol (II and III) and 1,5-dimethylbicyclo[3,3,1]non-2-en-9-one (X) in carbon disulphide (0·5 mm. cells). (*A*), Compound (II) (0·031M); (*B*), compound (III) (0·071M); and (*C*), compound (X) (0·026M).

FIG. 3. Solvent dependence of the carbonyl stretching absorptions of 1,5-dimethylbicyclo[3,3,1]nonane-2,9-dione (XI). (*A*), In hexane (0·011M; 0·51 mm. cell); (*B*), in chloroform (0·014M; 0·51 mm. cell).

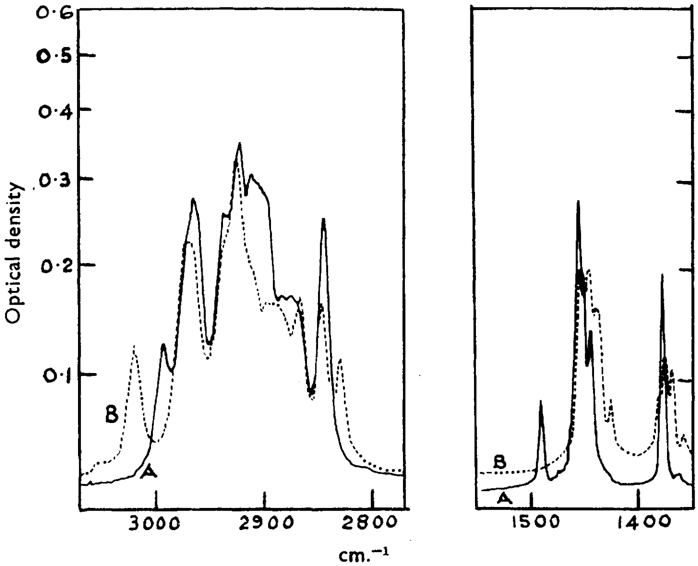


FIG. 4. C–H stretching and deformation absorptions of 1,5-dimethylbicyclo[3,3,1]nonan-9-one (IX) and 1,5-dimethylbicyclo[3,3,1]non-2-en-9-one (X) in carbon tetrachloride (0·51 mm. cell). (*A*), Compound (IX) (0·029M); (*B*), compound (X) (0·034M).

TABLE 5.

Abnormal methylene absorptions in carbon tetrachloride.*

No.	Compound	ν(C–H)	$\Delta\nu_{\frac{1}{2}}{}^{a}$	ε^{a}	δ(CH)	$\Delta\nu_{\frac{1}{2}}{}^{a}$	ε^{a}
(XIII)	1,5-Dimethylbicyclo[3,3,1]nonane	2990sh	(14)	60	1488	15	20
(I)	1,5-Dimethylbicyclo[3,3,1]nonan-9-ol	2991sh	(16)	80	1490	6	45
(IX)	1,5-Dimethylbicyclo[3,3,1]nonan-9-one	2992sh	(14)	70	1490	5	45
(IV)	2-Hydroxy-1,5-dimethylbicyclo[3,3,1]nonan-9-one	2994sh	(17)	75	1488	(8)	45
(XIV)	[2,3-$^{2}H_{2}$]1,5-Dimethylbicyclo[3,3,1]nonan-9-one	~2990 [e]	—	—	1473	—	(25)

* Concentrations were 0·05M, measured in 0·51 mm. cells, except for δ(C–H) of (IV) (0·001M, 2 cm. cell).

[b] Asymmetric band, broadening on low-frequency side. [c] Interference by strong carbonyl band. (For other abbreviations used in this and succeeding Tables, see Table1.) [d] Optical densities greater than 1, extinction values approximate. [e] Incompletely resolved shoulder.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus and are corrected; boiling points are uncorrected. Light petroleum refers to the fraction of b. p. 40—60° unless otherwise stated. Ultraviolet (u.v.) absorption spectra refer to ethanol solutions and were measured with a Unicam S.P. 500 spectrophotometer. Mass spectra were recorded with an A.E.I. M.S.9 double-focusing mass spectrometer. Infrared (i.r.) spectra were recorded linearly in cm.$^{-1}$ as percentage transmission with a Unicam S.P. 100 double-beam infrared spectrophotometer equipped with an S.P. 130 sodium chloride prism-grating double monochromator [3000 lines per inch (2000—3650 cm.$^{-1}$) and 1500 lines per inch (650—2000 cm.$^{-1}$)] operated under vacuum as described in the preceding Paper.

AnalaR carbon tetrachloride, carbon disulphide, and spectroscopic-grade n-hexane were used without purification. AnalaR chloroform was dried several times by passage through a column of blue silica gel immediately before use. Acetonitrile was purified by prolonged treatment with potassium hydroxide, calcium chloride, and phosphoric oxide, followed by distillation, and tetrachloroethylene by passage through a column of chromatographic silica gel.

Compounds Examined.—The preparations of (I—IV) and (X) have been previously described.[1] We are indebted to Dr. G. D. Meakins for compound (V), Dr. R. B. Clayton for compounds (VI) to (VIII) and to Professor H. Stetter for compound (XV).

1,5-*Dimethylbicyclo*[3,3,1]*nonan*-9-*one* (IX). A solution of 1,5-dimethylbicyclo[3,3,1]non-2-en-9-one [1] (X; 0·15 g.) in ethyl acetate (10 ml.) was hydrogenated over 10% palladium–charcoal (0·08 g.) for 1 hr. The solution was filtered with suction through Celite 535 and solvent removed under reduced pressure. The residue, a colourless volatile solid (0·13 g.) was sublimed to provide a pure sample of the *saturated ketone*, m. p. 49·5—50°, $\lambda_{max.}$ 290 mμ (ε, 22) (Found: C, 79·3; H, 10·7. $C_{11}H_{18}O$ requires C, 79·45; H, 10·9%). The mass spectrum showed a parent peak of 166 (Calc. 166).

[2,3-$^{2}H_{2}$]-1,5-*Dimethylbicyclo*[3,3,1]*nonane*-9-*one* (XIV). A solution of the ketone (X; 0·33 g.) in pure cyclohexane (10 ml.) was deuterated over 10% palladium–charcoal (0·25 g.) for 30 min. The solution was filtered with suction through Celite 535, and solvent removed under reduced pressure. The crude product (0·31 g.) was adsorbed on Woelm (neutral) alumina (4 g.) from light petroleum and eluted with the same solvent. The main fractions were recombined and sublimed to give needles of the *bisdeutero-ketone*, m. p. 50°. The mass spectrum showed a parent peak at 168 (Calc. 168), with small subsidiary peaks at 169 and 170, indicating incorporation of three and four deuterium atoms to a small extent.

1,5-*Dimethylbicyclo*[3,3,1]*non*-2-*ene* (XII). Zinc amalgam was prepared by shaking a mixture of zinc dust (20 g.), mercuric chloride (2 g.), water (10 ml.), and concentrated hydrochloric acid (1 ml.). The supernatant liquid was decanted and the amalgam washed with successive quantities of water. Water (10 ml.) was added to cover the amalgam, followed by the unsaturated ketone (X; 2·0 g.) and concentrated hydrochloric acid (25 ml.).

The mixture was refluxed with stirring for 30 hr., the solution decanted from the amalgam and combined with water and ether washings of the latter. The ether extracts were combined, washed with saturated sodium chloride solution, and sodium hydrogen carbonate solution, and dried. Removal of solvent at room temperature under reduced pressure gave the *olefin* (1·2 g.), which distilled as a mobile liquid, b. p. 60°/15 mm.; n_D^{24} 1·4708 (Found: C, 87·9; H, 11·95. $C_{11}H_{18}$ requires C, 87·9; H, 12·1%).

1,5-*Dimethylbicyclo*[3,3,1]*nonane* (XIII). A solution of (XII; 0·35 g.) in ethyl acetate (30 ml.) was hydrogenated over 10% palladium–charcoal (0·05 g.) for 30 min. The solution was filtered through Celite 535, the solvent removed at atmospheric pressure and the residue, a mobile oil, adsorbed on Woelm (neutral) alumina (5 g.) from light petroleum. Elution with the same solvent and molecular distillation of combined fractions gave the *saturated hydrocarbon*, b. p. *ca.* 180°/760 mm., n_D^{23} 1·4654 (Found: C, 86·5; H, 13·15. $C_{11}H_{20}$ requires C, 86·75; H, 13·25%).

1,5-*Dimethylbicyclo*[3,3,1]*nonane*-2,9-*dione* (XI). A solution of 2-hydroxy-1,5-dimethylbicyclo[3,3,1]nonan-9-one [1] (IV; 5·0 g.) in acetone (50 ml.) was cooled in ice and a slight excess of Jones reagent (8N-CrO_3 in dilute sulphuric acid) added dropwise with cooling. The mixture was diluted with water (200 ml.) and extracted with light petroleum (2 × 100 ml.). The combined petroleum extracts were washed with saturated sodium chloride solution, and saturated sodium hydrogen carbonate solution, and dried. Removal of solvent under reduced pressure gave a volatile solid (4·7 g.) which crystallised from light petroleum as prisms, m. p. 46—47°. Sublimation afforded a pure sample of the *diketone*, m. p. 47—48° (Found: C, 72·9; H, 8·55. $C_{11}H_{16}O_2$ requires C, 73·3; H, 8·95%).

DISCUSSION

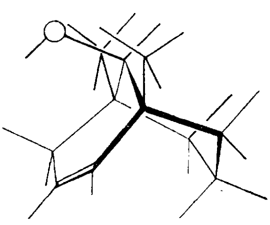
Hydroxyl Absorptions.—The hydroxyl stretching absorptions, measured in carbon tetrachloride solution at concentration levels low enough to eliminate intermolecular hydrogen bonding, are listed in Table 1. Even in dilute solutions we find an asymmetric ν(OH) band in the saturated bicyclo-alcohol (I), and this we believe to be due to conformational effects of the type discussed in recent Papers by Oki and Iwamura [2] and by Dalton, Meakins, Robinson, and Zaharia.[3] The compound (II), whose configuration is established below on the basis of the absence of intramolecular hydrogen bonding, also exhibits an asymmetric hydroxyl stretching absorption which must be due to the differing orientations of the OH bond.

The ν(OH) values for (I) and (II) are unusually high for secondary hydroxyls, probably an effect of steric crowding by the adjacent methyl groups.[4] (Values for phenol and 2,6-di-t-butylphenol, in carbon tetrachloride solution, are 3612 and 3647 cm.$^{-1}$, respectively.)

The configurational assignments for the alcohols (II) and (III) reported in Part III [1] were based on the finding that of the two epimers only one, the higher melting, exhibited a second and stronger ν(OH) absorption at 3584 cm.$^{-1}$ (Fig. 1). This spectral feature must be due to an intramolecular OH→π bond and thereby defines the relative orientation of the hydroxyl and double bond in this epimer, m. p. 80°, as *syn* (III; cf. XVI). Accordingly the other epimer, m. p. 55°, must be allocated the alternative, *anti*, configuration (II).

It is evident from the presence of the " free " band at 3640 cm.$^{-1}$, in the spectrum of (III), that although the hydroxyl group is *syn* to the double bond, there is present a small proportion of the conformer in which the –OH bond is pointing in the opposite direction. The possibility that this band was due to the presence of traces of the *anti*-epimer (II) has been eliminated by rigorous gas–liquid chromatographic analysis.

Related cases of OH→π bonding in unsaturated alcohols have been given by Schleyer *et al.*[5] and Oki and Iwamura,[2] for example but-3-en-1-ol shows a bonding shift (Δν) of 40 cm.$^{-1}$, while in the bicyclo[2,2,1]heptene system, a transannular interaction afforded a Δν of 30 cm.$^{-1}$, while the largest shift quoted (49 cm.$^{-1}$) referred to a tricyclic olefinic alcohol. In the present instance, the bands shown by compound (III) are separated by 56 cm.$^{-1}$. Dreiding models (XVI) indicate a distance of 2·9 Å between the oxygen and the centre of the carbon–carbon double bond. Similar OH→π bonding is evident in the data for compounds (VI—VIII) (Table 1). Introduction of either a 2,3- or a 7,8-double


(XVI)

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[2] Oki and Iwamura, *Bull. Chem. Soc. Jap.*, 1959, **32**, 567, 950.
[3] Dalton, Meakins, Robinson, and Zaharia, *J.*, 1962, 1566.
[4] Bellamy, Eglinton, and Morman, *J.*, 1961, 4762.
[5] Schleyer, Trifan, and Bacskai, *J. Amer. Chem. Soc.*, 1958, **80**, 6691.

bond[3] results in partial bonding with the 5α-hydroxyl group. It is of interest that there is complete bonding in the 7,9-diene (VIII), where the effect of the planarity induced by the conjugated system evidently outweighs the expected reduction in basicity of the π-electrons towards hydrogen bonding.

The above findings correlate well with the anomalous gas–liquid chromatographic retention factors reported by Clayton[6] for compounds (VI) and (VII), on poly(ethylene glycol succinate) columns. Suggestions that the low retention-times found for these compounds might be caused by either a blocking of the π electron–liquid phase interaction by the 5α-hydroxyl group, or by a transannular OH$\rightarrow\pi$ bond. Our belief that the latter effect is dominant gains support from similar data[1] for the alcohols (I)—(III), on a 5% poly(ethylene glycol) column. The *syn*-epimer (III) had a retention time of 9·7 min., compared with 14·3 min. for the *anti*-epimer (II), and 14·4 min. for the saturated alcohol (I), under the same conditions. The last two results indicate that the hydroxyl grouping, and not the π-electrons, plays the more significant role in bonding to the liquid phase.

Incidentally, the stereochemistry of compound (IV), which has been established unambiguously,[7] might seem to permit intramolecular OH$\rightarrow$O=C hydrogen bonding, but Dreiding models show that the distance from the oxygen to the carbonyl double bond is too great (slightly in excess of 3 Å), and this hydroxyl frequency is normal (Table 1).

Two further series of measurements have been employed to confirm the intramolecular bonding in (III). Dilute solutions of this epimer in tetrachloroethylene showed that the intra-bonding band decreased in intensity relative to the " free " band as the temperature was raised, ($\varepsilon_{\text{intra}}/\varepsilon_{\text{free}}$ was 2·8, 2·3, and 1·7 at 25, 50, and 80°, respectively, the frequencies and half-band widths remaining approximately constant, cf. ref. 3). It was also possible to disrupt the intra-molecular OH$\rightarrow\pi$ bond by adding ether to the carbon tetrachloride solution of epimer (III), whereupon a new broad band appeared (Fig. 1) at 3505 cm.$^{-1}$ ($\Delta\nu^{a}_{\frac{1}{2}} \sim 90$ cm.$^{-1}$) which increased in intensity with increasing ether concentrations. The formation of such a solvent complex, $-\text{OH}\rightarrow\text{O}<$ is interesting in view of the steric congestion around the 9-hydroxyl function.

The ν(C–O) absorptions of the alcohols (I—III) were also measured in carbon tetrachloride solutions. The spectrum of the saturated alcohol (I) exhibited a main band at 1068, and a subsidiary one at 1038 cm.$^{-1}$. In this molecule, the OH group is simultaneously axial and equatorial on a cyclohexane ring, and no real correlation can be made with the results of Jones *et al.*[8] who have found that equatorial 3-hydroxy-steroids give rise to ν(C–O) bands of higher frequency than those of the corresponding axial alcohols. Similarly the carbon–oxygen stretching bands in compounds (II) (1052 cm.$^{-1}$) and (III) (main band at 1060; subsidiary, 1020 cm.$^{-1}$) cannot be used reliably for configurational assignments.

Olefinic Absorptions.—There is only one possible 1,5-dimethylbicyclo[3,3,1]nonene (XII), and Table 2 summarises the ν(CH), ν(C=C), and γ(CH) absorptions for this compound and for various 9-substituted analogues. In general, this *cis*-disubstituted double bond shows absorption frequencies similar to those of the double bond of cyclohexene, except that the bands are much sharper and better defined, a fact which we attribute to the rigidity of the fused cyclohexenyl system. There are no indications, however, of any shifts attributable to the introduction of ring strain. It is generally agreed[9] that rigorous correlations cannot be drawn between the absorption patterns and environments of *cis*-double bonds, as there is often an unexplained multiplicity of bands.

The olefinic CH stretching absorptions are very similar in all four compounds, and are typified by the band at 3019 cm.$^{-1}$ for compound (X) (Fig. 4). Two weak bands near 1650 and 1635 cm.$^{-1}$ are observed; this dual absorption presumably originates in Fermi

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[6] Clayton, *Nature*, 1961, **192**, 524.

[7] J. Martin and W. Parker, forthcoming publication.

[8] Cole, Jones, and Dobriner, *J. Amer. Chem. Soc.*, 1952, **74**, 5571.

[9] Henbest, Meakins, and Wood, *J.*, 1954, 800; Henbest, Meakins, Nicholls, and Wilson, *J.*, 1957, 997.

resonance involving ν(C=C) rather than conformational heterogeneity. The asymmetry of the doublet in (III), however, and the lower intensities, are suggestive of further splitting arising from the presence of the intra-bonded and non-bonded conformers already discussed. The out-of-plane CH deformations occur near 710 cm.$^{-1}$ and are generally sharp and intense. The saturated alcohol (I) is virtually transparent between 820 and 650 cm.$^{-1}$, thereby obviating any ambiguity. Compounds (II) and (XII) (Fig. 2) exhibit a single, sharp maximum at 710 cm.$^{-1}$, comparable in intensity with the combined extinction coefficients for the multiplets noted by Henbest *et al.*[9] for *cis*-double bonds in steroids and related systems. In contrast, the *syn*-alcohol (III) (Fig. 2) has a somewhat broader and less intense γ(CH) band which may be associated with the intramolecular bonding. This effect, though admittedly small, would be analogous to the changes produced by metal ion→π-bond complex formation.[10] Changes in the γ(CH) absorption can be induced by a number of factors; for example, the ketone (X) (Fig. 2) shows two bands at 719 and 696 cm.$^{-1}$, the splitting being attributable to the presence of the polar oxygen function.[9]

Carbonyl Stretching Absorptions.—The carbonyl stretching absorption of the compounds studied are listed in Table 3. The absorptions are approximately those to be expected for a six-ring ketone in the case of (IX), (X), and (IV), but the diketone (XI) shows a well-defined double peak (Fig. 3). This splitting we ascribe to vibrational coupling of the type fully described for anhydrides and peroxides,[11] since the band separation and relative intensities are virtually solvent-independent (Table 4). The fact that the higher frequency band is the weaker of the two is in accord with the geometry of the molecule whereby the disposition of the carbonyl groups may be likened to that of a glutaric anhydride, although the –CO–C–CO– system cannot be planar. Finally, the carbonyl absorption of compound (XV) is unusually high in frequency, presumably because a likely stable conformation of this molecule would involve the carbonyl groups being parallel and pointing in the same direction; the dipolar interaction would result in enhanced ν(C=O) values.

Methylene CH *Stretching and Bending Absorptions.*—Models of the saturated bicyclo[3,3,1]nonane system show that no matter which conformation the molecule adopts [conformational sketches XVII (a)—(d)] there exist strong non-bonded hydrogen–hydrogen interactions. Evidence of such interactions in the 1,5-dimethyl series has been afforded by an examination of the CH stretching and bending regions in the infrared region (Fig. 4). Of the compounds examined (I—IV, IX—XV), five (Table 5) show absorption near 2990 and 1490 cm.$^{-1}$, though in saturated compounds these regions are generally free from absorption. De Vries and Ryason [12] have found ν(CH) bands at abnormally high frequencies (3055—2980 cm.$^{-1}$) in a variety of fused polycyclic compounds in which two or more methylene groups are forced into close proximity. The bands are generally rather indistinct shoulders on the high-frequency side of the main ν(C–H) absorption and assignment is difficult when the molecule contains double bonds; confusion is possible with olefinic ν(C–H) bands. In the bicyclo-series, the 1490 cm.$^{-1}$ bands would appear to be more diagnostic as they are well separated from the normal methylene scissoring absorption. The i.r. spectra of pertinent bicyclo[3,3,1]nonane compounds reported by Stoll *et al.*[13] also show high frequency scissoring bands.

Chiurdoglu *et al.*[14] have classified the methylene scissoring absorptions, δ(CH_2), of alicyclic hydrocarbons, ketones, and alcohols (C_5—C_{17}) in terms of both the number of distinct bands and the frequency differences between the highest and lowest, their intention being to estimate the number of different types of methylene and the degree of interaction. They go on to suggest that cyclo-octane, -nonane, and -decane exist as single preferred conformations in solution. The bicyclo[3,3,1]nonane system may be thought of as a bridged

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[10] Powell and Sheppard, *Spectrochim. Acta.*, 1958, **13**, 69.

[11] Bellamy, Connelly, Philpotts, and Williams, *Z. für Electrochemie*, 1960. **64**, 563.

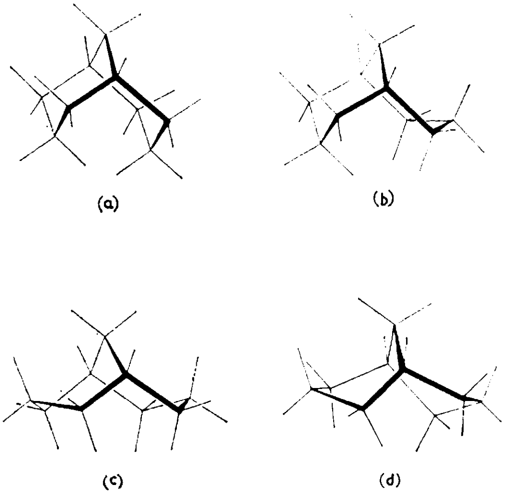
[12] De Vries and Ryason, *J. Org. Chem.*, 1961, **26**, 621.

[13] Stoll, Willhalm, and Büchi, *Helv. Chim. Acta.*, 1955, **38**, 1573.

[14] Chiurdoglu, Doehaerd, and Tursch, *Bull. Soc. Chim. France*, 1960, **69**, 1322; *Chem. and Ind.*, 1959, **9**, 1453.

cyclo-octane derivative. Indeed the " skewed crown " conformation suggested for this compound [14,15] merely requires formal replacement of two transannularly opposed 1,5-hydrogens by a bridging methylene group, the result being the twin-boat conformation (XVIIc), whereas the folded conformation suggested by Dale [16] for cyclo-octane would similarly give rise to the twin-chair conformation (XVIIa). Chiurdoglu *et al.* found a difference of 27 cm.$^{-1}$ between the highest and lowest frequency methylene-scissoring bands of cyclo-octane. Unfortunately, it has not proved possible to give definitive $\Delta\delta(CH_2)$ values in the present instance, as most of the five compounds show a main band with shoulders. If the shoulders appearing near 1432 cm.$^{-1}$ are regarded as the lowest-frequency bands, then $\Delta\delta(CH_2)$ is 55 cm.$^{-1}$, but if the main $\delta(CH_2)$ value is used (mean, 1455 cm.$^{-1}$), the value of $\Delta\delta(CH_2)$ is 35 cm.$^{-1}$. The highest values 43 and 38 cm.$^{-1}$, recorded by Chiurdoglu *et al.* were for C_9 and C_{10} rings, respectively, matching the degree of congestion encountered in these alicyclic rings.

It would seem that the high-frequency band is associated with the interacting methylenes, and in our series we believe that these are the 3- and 7-methylenes on the grounds that they show closest approach, in conformation (XVIIa), and that any change in the molecule which relieves this interaction, as in compounds (II), (III), (X), (XI), (XII), and (XV), results in the disappearance of the band at 1490 cm.$^{-1}$. All the conformations depicted involve unfavourable hydrogen–hydrogen interactions to some extent, but the molecule must adopt one (or more) of them, or at least something closely similar. Quite serious interactions between hydrogens in crowded structures are known to be tolerated, by distortion either of the carbon framework or of the C–H bonds involved.


(a) (b) (c) (d)

(XVII a–d)

The possible conformations of the bicyclo[3,3,1]nonane skeleton, and the more serious interactions involved therein, may be described briefly as follows:

(XVIIa). In this " twin-chair " conformer, one very serious interaction occurs between the *endo*-hydrogens on $C_{(3)}$ and $C_{(7)}$. From a Dreiding model composed of ideal chairs, the H–H internuclear distance is 0·8 Å, but in reality this conformer would, of necessity, be distorted to accommodate these hydrogens.

(XVIIb). Relief of the 3–7 methylene interaction could be brought about if the molecule assumed the " boat–chair " form, but the creation of a 3,9 " bowsprit " interaction in the boat, and also 3,6- and 3,8-hydrogen interactions of comparable severity below the molecule, would offset the easement of crowding.

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[15] Allinger and Shih-En-Hu, *J. Amer. Chem. Soc.*, 1961, **83**, 1664.
[16] Dale, *J.*, 1963, 93.

(XVIIc). Consideration of a " twin-boat " conformer cannot be excluded in such an inescapably crowded system. In addition to the obvious 3,9- and 7,9-interactions, two less serious ones between the 2,8- and 4,6-hydrogens must be considered.

(XVIId). The ideal " twin-boat " conformer is the only one which has any rotational freedom in the carbon framework, and permissible distortion produces this " twin-twist boat " conformer. A slight, but probably negligible, relief of the bowsprit interactions is accompanied by the creation of a serious transverse 2,6-interaction below the rings as they are depicted.

If we assume that the band at 1490 cm.$^{-1}$ is indeed an indication of an unusually serious methylene–methylene interaction, then we can eliminate all but the twin-chair form (XVIIa) as dominant conformer on the grounds (*a*) that compound (IX) has the 1490 band (Fig. 4), thereby eliminating $C_{(3)}$–$C_{(9)}$ and $C_{(7)}$–$C_{(9)}$ interactions, and (*b*) that the intensity of this band is approximately the same whether a compound has a trigonal or a tetrahedral configuration at $C_{(9)}$ (indicating that 3—9 and 7—9 interactions are unimportant). In an attempt to confirm that the 3- and 7-methylene groups are responsible for the abnormally high frequency bands at 2990 and 1490 cm.$^{-1}$, we prepared the bisdeutero-ketone (XIV).

In this compound we expected the substitution of a CDH grouping in the 3-position to affect the intensities of both abnormal bands. In the event, the spectrum (Table 5) showed a reduction, of approximately one-half in the intensity of the 1490 cm.$^{-1}$ band, an effect attributable to the replacement of the H–C–H scissoring band of the 3-methylene group by a D–C–H scissoring absorption elsewhere in the spectrum. Correspondingly, the 2990 cm.$^{-1}$ band appeared as an indistinct shoulder on the high frequency side of the main C–H stretching absorption (cf. IX; Fig. 4 and Table 5). The appearance of an additional weak band at 1473 cm.$^{-1}$ may be an indication of the effect of the deuterium atom on a coupled vibration mode of the two groups of three atoms. In addition, *endo*-3-hydroxy-1,5-dimethylbicyclo[3,3,1]nonane, in which the steric requirements of the hydroxyl group demand modification of the twin-chair conformation, does not exhibit the 1490 and 2990 cm.$^{-1}$ bands. Analysis of available data indicates that the hydroxyl-bearing ring exists as a boat form. A further check on the authenticity of our assignment for the 1490 cm.$^{-1}$ band was obtained from the infrared spectrum of adamantane,[17] which shows no significant absorption there; this compound is clearly analogous, in its stereochemistry, to the twin-chair conformer (XVIIa), and is formally derivable by insertion of one methylene group between carbons 3 and 7, thereby eliminating the 3,7-methylene hydrogen–hydrogen interaction.

To summarise our conclusions, we believe that bicyclo[3,3,1]nonane and, in particular, the 1,5-dimethyl compounds which we have studied, exist in distorted twin-chair conformations, where the 3,7-transannular hydrogen interactions are relieved either by carbon–carbon bond-angle changes as in the medium-sized carbocycles, or by localised H–C–H bond-angle disturbances. The infrared spectral bands which we attribute to the 3,7-methylene crowding appear both in solution and the solid state thereby permitting the extrapolation of *X*-ray crystallographic results to molecular shape in solution. The diffraction analysis of a bicyclo[3,3,1]nonane derivative, reported recently by us in collaboration with Brown and Sim,[18] has confirmed our findings.

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[17] Mecke and Spiesecke, *Chem. Ber.*, 1955, **88**, 1997.

[18] Brown, Eglinton, Martin, Parker, and Sim, *Proc. Chem. Soc.*, 1964, 57.