

817. *The Vibrational Spectrum of Bicyclo[2,2,2]octane.*

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The infrared and polarized Raman spectra of bicyclo[2,2,2]octane have been recorded. The spectra are consistent with those predicted on the assumption that the molecular symmetry is D_{3h} , *i.e.*, that the molecule is not twisted about its 3-fold axis. A substantially complete set of fundamental frequencies is proposed, partly based upon, and in reasonable accord with, values predicted for the skeletal frequencies by treating the CH and CH₂ groups as mass points and using without change the elastic constants proposed by Larnaudie for cyclohexane.

BICYCLO[2,2,2]OCTANE (I) is a saturated bicyclic hydrocarbon, rigid yet unstrained, whose high symmetry makes possible an unusually convincing analysis of the vibrational

spectrum. The consequent possibility of determining a really convincing force field is of far-reaching importance for the spectra of saturated hydrocarbons in general. The Raman spectrum has already been measured by Kohlrausch *et al.*,¹ and rather tentatively interpreted on the basis of a severely simplified normal co-ordinate analysis of the skeletal frequencies (Wagner²). The present work comprises further Raman measurements (including polarization data), a study of the infrared absorption, a rather more comprehensive calculation of the skeletal frequencies, and a reassignment of the spectrum.

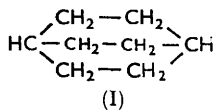


TABLE I. *Vibrational species of bicyclo[2,2,2]octane (D_{3h} model).*

| | A_1' | A_1'' | A_2' | A_2'' | E' | E'' | Freq. (cm. ⁻¹) |
|--------------------------------------|--------|---------|--------|---------|------|-------|----------------------------|
| Skeletal | 3 | 1 | — | 2 | 3 | 3 | < 1300 |
| CH: stretch | 1 | — | — | 1 | — | — | ca. 2900 |
| deformation | — | — | — | — | 1 | 1 | ca. 1350 |
| CH ₂ : sym. stretch | 1 | — | — | 1 | 1 | 1 | ca. 2950 |
| asym. stretch | — | 1 | 1 | — | 1 | 1 | ca. 2860 |
| bend | 1 | — | — | 1 | 1 | 1 | ca. 1450 |
| wag | 1 | — | — | 1 | 1 | 1 | 1150—1350 |
| rock | — | 1 | 1 | — | 1 | 1 | 1150—1350 |
| twist | — | 1 | 1 | — | 1 | 1 | 750—1100 |
| Total 1500 cm. ⁻¹ | 5 | 3 | 2 | 4 | 8 | 8 | |

Selection rules.*

| | | | | | | |
|----------------|------|------|------|-------------|---------|------|
| Raman | p | ia | ia | ia | dp | dp |
| Infrared | ia | ia | ia | \parallel | \perp | ia |

* p : polarized; dp : depolarized; ia : inactive.

Table I summarizes the predicted features of the spectrum. The assumed symmetry is D_{3h} , though we are also obliged to entertain the possibility that the molecule is slightly twisted about its 3-fold axis; such a deformation would reduce the repulsions between the hydrogen atoms of adjacent methylene groups, at the expense of straining the C-C bond structure. Such twisted conformations (there are right- and left-handed forms) have symmetry D_3 . For point-group D_3 the distinction in Table I between singly and doubly primed (*e.g.*, A_1' and A_1'') representations disappears, and the appropriate predictions are made by adding the columns of the Table together in pairs. Table I then indicates, in particular, that for D_{3h} (D_3) symmetry there are expected, below 1500 cm.⁻¹, 5 (0) completely inactive fundamentals, 12 (22) fundamentals active in the infrared, and 21 (25) in the Raman region; of these 8 (16) should be active in both types of spectrum.

EXPERIMENTAL

The bicyclo-octane was a synthetic sample, m. p. 168—171°, prepared by Dr. H. M. Walborsky and Dr. D. F. Loncrini.³ After vacuum-sublimation it formed small, detached, soft, very slightly sticky crystals.

The Raman spectrum, excited with Hg 4358 Å radiation (filtered with saturated sodium nitrite solution), was recorded with a Hilger photoelectric Raman spectrometer. The spectral band-width was 6 cm.⁻¹. The error in the frequencies of sharp lines is estimated at ± 2 cm.⁻¹. Measurements were made on 30% solutions (by weight) in carbon tetrachloride and in benzene. Polarization measurements were carried out according to the procedures described by Cranmer and Werner.⁴

Our measurements, which are included in Table 2, essentially confirm those of Kohlrausch *et al.*,¹ and add the polarization data. Only two bands are definitely polarized, but the spectrum is very weak and any of the bands whose intensity is less than 2, on the arbitrary scale used in the Table, could in fact be polarized.

¹ Kohlrausch, Seka, and Tramposch, *Ber.*, 1942, **75**, 1385.

² Wagner, *Z. phys. Chem.*, 1941, **B**, **48**, 316.

³ Walborsky and Loncrini, *J. Amer. Chem. Soc.*, 1954, **76**, 5396.

⁴ Cranmer and Werner, *Austral. J. Chem.*, 1957, **10**, 87.

TABLE 2. Vibrational frequencies of bicyclo[2,2,2]octane (cm.⁻¹).

| Raman Soln. | Infrared | | | | Assignment |
|-------------|----------------------|--------|---------|--------|--|
| | Vapour | Mull | Solid | Soln. | |
| 371(1) | —* | — | 352vw † | — | skel. (E') |
| | — | — | 384?vw | — | skel. (E'') |
| 603(00?) | — | 522vw | — | — | skel. (E'') |
| | — | 610vw | — | — | 958—352 |
| | — | 635vww | — | — | 1010—371 |
| | | | 672vw | — | ? |
| | | 680w | 680w | — | skel. (A ₁ ') |
| | | 711vw | 710vw | — | 1228—522 |
| | | 734vw | 733vw | — | 1093—371 |
| | | | 765vww | — | 1134—371 |
| 795(10); p | | | | | skel. (A ₁ ') |
| | 796m | 798m | — | 797m | rock (E') |
| | 820w | 820m | — | 819m | skel. (E') |
| 863(½) | 868 ^q s ‡ | 869s | — | 868s | skel. (A ₂ '') |
| | | 906vw | 905vw | — | 1271—371 |
| | | 950vw | 950vw | — | 1299—352 |
| 958(½) | | 960vw | 960vw | — | rock (A ₁ ' or A ₂ '') |
| | | 977w | — | — | ? |
| | 989 ^q m | 988m | — | 988m | skel. (A ₂ '') |
| 1014(3) | 1010w | 1003w | — | — | skel. (E') |
| 1050(3) | | | — | — | skel. (E'') |
| 1093(4) | | 1102w | — | 1102w | rock (E'') |
| | | 1134w | — | 1134w | rock or wag |
| 1159(2); p | | 1163w | — | — | skel. (A ₁ ') |
| 1228(4) | | | — | — | wag (E') |
| | 1244w | 1239m | — | 1236m | wag (E') |
| | 1271 ^q s | 1269s | — | 1268s | wag (A ₂ '') |
| | | 1299vw | — | — | twist |
| | | 1314vw | — | — | twist |
| 1343(1) | | 1341m | — | 1342m | CH def. |
| 1350(1) | | 1351m | — | 1351m | twist (E' or E'') |
| 1438(4) | | — | — | — | bend |
| 1443(4) | 1464vs | — | — | 1457vs | bend |

(The following bands, all vw, were observed in the solid only: 1624, 1677, 1730, 1772, 1825, 1850, 1955, 1970, 2005, 2035)

| | | | | | |
|---------|-------------------------|-------|---|---------|--|
| | 2485w | 2485w | — | 2490w | |
| | | 2545w | — | — | |
| | 2590m | 2580m | — | 2580m | combinations, etc., not convincingly assignable |
| | 2655s | 2650s | — | 2655s | |
| | | 2670w | — | — | |
| | | | — | 2790m | |
| 2863(½) | | — | — | — | symm. CH ₂ stretch (A ₁ ') |
| | 2867 | | | | |
| | 2875 ^q } vvs | — | — | 2870vvs | symm. CH ₂ stretch (E') |
| | 2884 } vvs | — | — | — | CH stretch (A ₂ '') |
| | 2921vs | — | — | — | |
| | 2934 | | | | |
| | 2942 ^q } vvs | — | — | 2935vvs | asymm. CH ₂ stretch (E') |
| | 2950 | | | | |
| 2964(3) | | | | | asymm. CH ₂ stretch (E'') |
| | 3195m | 3190m | — | 3200m | |
| | 3310m | 3305m | — | 3310m | |
| | 3410m | 3415m | — | 3420m | |

* A dash (—) means unobserved for experimental reasons (too intense, interferences by solvents, etc.). A blank means no band observed in fact.

† w = weak, m = medium, s = strong, v = very.

‡ ^q denotes a vapour absorption band with a pronounced Q branch.

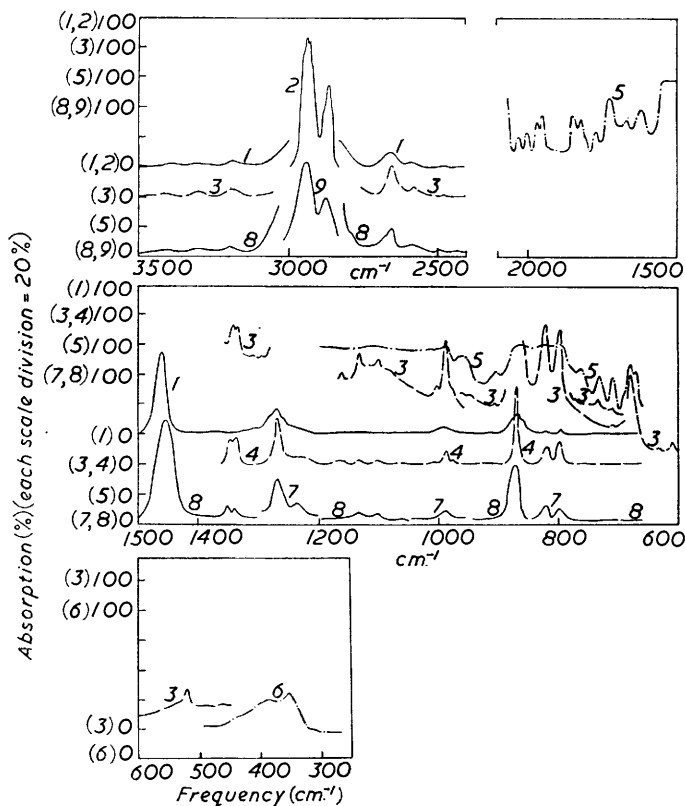
Infrared absorption measurements (Fig. 1) over the range 3900—600 cm.⁻¹ were carried out by using a Perkin-Elmer Model 12C (single-beam) spectrometer with 60° calcium fluoride and sodium chloride prisms. The wavelength scale was calibrated against the characteristic bands of several gases and vapours, and also by the method of Downie *et al.*⁵ Measurements from 600 to 250 cm.⁻¹ were made on a Perkin-Elmer Model 112 (double-pass) instrument, with 60°

⁵ Downie, Magoon, Purcell, and Crawford, *J. Opt. Soc. Amer.*, 1953, **43**, 941.

potassium bromide and 20° caesium bromide prisms, calibrated against the vapour absorption bands of water and methanol, and the values given by Plyler⁶ for aromatic hydrocarbons. Frequent recalibrations were routine.

In the vapour phase the 10 cm. heated cell used sufficed to locate only the stronger bands; in addition to the usual solution spectra, measurements were made on pressed discs of the solid. Such discs were lightly coated with paraffin and enclosed between windows to obviate sublimation in the infrared beam.

FIG. 1. Infrared spectra of bicyclo[2,2,2]octane.



- Vapour, 10 cm. path, 125°. (1) 0.68 g./l.; (2) 0.025 g./l.
 - - - Paraffin mull (solid). (3) thickness 0.3–0.4 mm.; (4) thin film.
 . . . Solid. (5) thickness approx. 1 mm.; (6) approx. 3 mm.
 — Soln., 0.1 mm. path. (7) in CS₂, 1.39M; (8) in CCl₄, 1.64M; (9) in CCl₄, 0.16M.
 Prisms: 3500–2400 (CaF₂); 2100–650 (NaCl); 670–450 (KBr); 500–250 cm.⁻¹ (CsBr).

Table 2 lists the observed frequencies.

Assignments.—The vibrational spectrum of bicyclo-octane shows relatively few bands in the fundamental region, and in particular only about 8 coincidences between Raman and vapour or solution infrared frequencies. This happens to be the number predicted on the D_{3h} model, though this is somewhat coincidental in view of experimental uncertainties, in the low-frequency region especially. Nevertheless, the comparative simplicity of the spectrum is wholly compatible with the D_{3h} (non-twisted) molecular conformation. True, if the twisting were slight, the selection rules would be inconsiderably broken down, and the spectral consequences would be hard to recognise. The skeletal twisting frequency itself, which would be expected to show torsional doubling were the equilibrium conformation D_3 , is inaccessible in the infrared, and presumably excessively weak in the Raman spectra, and no combination tones involving it have been identified. Slight twisting, however, would scarcely affect the validity

⁶ Plyler, *Discuss. Faraday Soc.*, 1950, 9, 100.

of the frequency calculation upon which many of the assignments are based, and we consider ourselves justified in proceeding on the basis of the untwisted model.

In the low-frequency region ($<1500\text{ cm}^{-1}$) only four bands can be immediately identified: the three strong bands near 1450 cm^{-1} are undoubtedly CH_2 bending frequencies, and Kohlrausch's identification of the intense Raman line at 795 cm^{-1} as the skeletal breathing mode (A_1') is confirmed by its strong polarization. This band is accidentally coincident with a pronounced infrared frequency (vapour: 796 cm^{-1}) which we identify with an expected strong CH_2 rocking frequency. Analogous molecules may be cited: cyclohexane in this vicinity has only one band (802 cm^{-1}), identified by Larnaudie⁷ as a skeletal frequency and by Beckett, Pitzer, and Spitzer⁸ as a superposition of skeletal and rocking frequencies. Mecke and Spiesscke⁹ assign as rocking modes bands at 799 cm^{-1} in hexamine and 812 cm^{-1} in adamantane. In quinuclidine, $^2\text{CH} \left\langle [\text{CH}_2 \cdot \text{CH}_2]_3 \right\rangle \text{N}$, and triethylenediamine, $^{10}\text{N} \left\langle [\text{CH}_2 \cdot \text{CH}_2]_3 \right\rangle \text{N}$, these rocking frequencies are probably at 780 and 775 cm^{-1} respectively.

The remaining bands have to be identified by analogy with other molecules or from the results of trial calculations, for no help is available from polarized infrared measurements (the crystal structure of bicyclo-octane is unknown, but in any event is probably disordered since the molecule is almost spherical), and next to none from band contours. In the latter connection we note that the molecule is a symmetric, almost spherical, top ($I_A = I_B = 346$, $I_C = 354 \times 10^{-40}\text{ g. cm}^2$); equal statistical weights being assumed for all rotational levels (their variation is only 2%), Gerhard and Dennison's formulæ¹¹ predict that both parallel and perpendicular bands should show moderately well-defined Q branches, and a P - R branch spacing of from 16 cm^{-1} (300° K) to 19 cm^{-1} (400° K), precisely as observed (Fig. 1). Dr. N. Sheppard has pointed out to us that the definition of the Q branch might be expected to be impaired in the perpendicular bands because of Coriolis interaction; however, our vapour spectra are rather weak and it is difficult to be sure that the bands do in fact fall into two classes with a characteristic difference in Q -branch resolution.

TABLE 3. Calculated skeletal frequencies of bicyclo[2,2,2]octane (cm^{-1}).

| Symmetry | A * | B * | Obs. | Symmetry | A * | B * | Obs. |
|---------------|-------|-------|------|-------------|-------|-------|------|
| A_1' | 1190 | 1166 | 1159 | E' | 1266 | 981 | 1010 |
| | 785 | 785 | 795 | | 1003 | 847 | 820 |
| | 516 | 667 | 680 | | 450 | 337 | 352 |
| A_1'' | 256 † | 204 † | — | E'' | 1280 | 1058 | 1050 |
| A_2'' | 913 | 936 | 989 | | 658 | 535 | 522 |
| | 836 | 897 | 868 | | (371) | (371) | 371 |

* Force constants used in these calculations are specified in the text. † Highly uncertain; see text.

Calculations of the frequencies (see Appendix) were restricted to the skeletal modes, and used force constants transferred from other alkanes. We quote, in Table 3, the results of two such calculations, together with our eventual identifications of the skeletal frequencies. Calculation A used an excessively simple force field, rather similar to that of Kohlrausch *et al.*;¹ namely, the diagonal force constants $f_r = f_s$, $f_\alpha = f_\beta$, f_τ (cf. notation in Appendix) for stretching, bending, and torsion were given the values 4.5 , $0.50r^2_{\text{CC}}$, $0.13r^2_{\text{CC}}\text{ md}/\text{\AA}$, respectively, and all interaction constants were set equal to zero. Calculation B used as far as possible the force constants, which include four interaction constants, derived by Larnaudie⁷ in his complete treatment of cyclohexane (in particular, $f_r = f_s = 4.5$, $f_\alpha = f_\beta = 0.55r^2_{\text{CC}}\text{ md}/\text{\AA}$); additionally f_τ was $0.087r^2_{\text{CC}}\text{ md}/\text{\AA}$ and an interaction constant between adjacent CCC bends at the tertiary carbon atoms of $0.28r^2_{\text{CC}}\text{ md}/\text{\AA}$ (suggested by Larnaudie's figures) was also included. The values of f_τ were chosen to fit 371 cm^{-1} as the lowest E'' frequency; as a result f_τ is closely linked to f_α , and the calculated values of the lone A_1'' frequency (the molecular twisting mode), which is determined solely by f_τ , are extremely tentative. It is at once clear that the simple force field A gives results for the higher skeletal frequencies which are probably much too high, and accordingly these predictions were given little weight. The force field which Ramsay and Sutherland applied to cyclohexane (it includes a very low value for f_τ , *viz.*, 3.69×10^5 dynes

⁷ Larnaudie, *Compt. rend.*, 1952, **232**, 316; *J. Phys. Radium*, 1954, **15**, 365.

⁸ Beckett, Pitzer, and Spitzer, *J. Amer. Chem. Soc.*, 1947, **69**, 2488.

⁹ Mecke and Spiesscke, *Spectrochim. Acta*, 1956, **7**, 387.

¹⁰ Personal communication from Dr. N. Sheppard.

¹¹ Gerhard and Dennison, *Phys. Rev.*, 1933, **43**, 197.

cm.⁻¹) likewise gave most unlikely results (*e.g.*, 711 cm.⁻¹ for the breathing mode) which are not reproduced here, nor are various other calculations, designed to explore the sensitivity of the frequencies to the assumed elastic constants (of which the two sets of calculated E' frequencies in Table 3 afford ample evidence). Nor, finally did we seriously attempt to adjust the calculated frequencies to our final assignments, since we feel such an adjustment would be meaningful only when carried out as part of a complete calculation.

Proceeding again with the assignments, we next identify 868 and 989 cm.⁻¹ as A_2'' skeletal modes. The evidence is the intensity and contours of the infrared bands. They do not agree well with the calculated frequencies, but their separation in the Larnaudie calculation (B of Table 3) is particularly small in comparison with all other calculations. If these assignments are correct then the weak Raman line at 863 cm.⁻¹ is either a different vibration, or is to be attributed to a breakdown of the isolated molecule selection rules.

Below 795 cm.⁻¹ we expect only five skeletal fundamentals, of which one (A_1'') is forbidden and is probably inaccessibly low. The other four are hard to identify positively; in particular, we are by no means convinced of the authenticity of the 603 cm.⁻¹ Raman line [like Kohlrausch *et al.*, we mark its intensity as (00?)], and while there is undoubtedly some absorption in the vicinity of 370 cm.⁻¹, the high dispersion and rapidly varying intensity of the reference spectrum (a single-beam instrument was used) make it difficult to be sure that there are really two distinct frequencies here; the assignments nevertheless assume this. For the A_1' and the second E'' frequencies there is little evidence other than the calculations.

The higher frequencies are fairly straightforwardly assigned and the identifications of the skeletal frequencies are uniformly reasonable. The pair of bands at 1343, 1350 cm.⁻¹ should include the CH deformation and a CH₂ twist. The former is a rather obscure frequency in most paraffin spectra, and the trio of compounds, bicyclo-octane, quinuclidine, and triethylenediamine, affords a unique opportunity of locating it. Quinuclidine has a Raman line at 1348 cm.⁻¹; triethylenediamine an infrared band at 1354 cm.⁻¹. The persistence of a frequency near to 1350 cm.⁻¹ throughout this sequence leads us to the assignments 1350 cm.⁻¹ (twist) and 1343 cm.⁻¹ (CH deformation) in bicyclo-octane. In labelling the remaining CH₂ frequencies we have assumed, with previous authors,^{7,8} that wagging frequencies in cyclic alkanes are lower than twisting ones, and we have suggested symmetries for these frequencies when the selection rules, or a process of elimination, provide reasons.

Of the bands below 1500 cm.⁻¹ which are not regarded as fundamentals, all but two are plausibly identified as difference frequencies; the fit in each case is within experimental error.

In the region of the CH₂ stretching frequencies there are two distinct absorption regions in the infrared vapour spectrum. The symmetric stretching region (~ 2870 cm.⁻¹) is expected to contain two infrared frequencies (A_2'' and E'); however, the observed absorption (maximum at 2875 cm.⁻¹) appears to be a single band, with P and R branch shoulders at their expected spacing of 17 cm.⁻¹. An elementary calculation predicts that the E' frequency should be about four times as intense as A_2'' which it presumably submerges. The sole observed Raman line, at 2863 cm.⁻¹, we take to be A_1' , again on intensity grounds. The infrared band in the asymmetric stretching region contains a fourth shoulder (2921 cm.⁻¹); since only one CH₂ frequency (E') is expected to be infrared active this shoulder must be the CH stretching mode; the expected location of its frequency (2890—2900 cm.⁻¹) appears to be clear of absorption. The single asymmetric Raman mode, being not coincident with the infrared frequency, must be E'' . It will be remarked that all these stretching frequencies are some 20—30 cm.⁻¹ higher than in cyclohexane and acyclic alkanes.

DISCUSSION

It was the aim of the present work to determine a set of assignments for bicyclo-octane upon which a more extensive normal co-ordinate analysis might be based. Inasmuch as the calculated frequencies (Table 3, col. B) have considerably influenced our assignments, it may seem specious to claim that the agreement with experiment (root-mean-square deviation over 10 frequencies: 24 cm.⁻¹) is quite good for a completely *a priori* force field. Yet the alternative frequency patterns which most deserve consideration are those in which, as Table 3, col. A suggests, the upper limit of the skeletal frequencies is appreciably raised (Kohlrausch *et al.*¹ assumed this). Such an assignment might begin with the identification of the strong 1271 cm.⁻¹ infrared vapour frequency as an E' skeletal mode.

The assignments which we devised on such bases were consistently less satisfactory than that proposed here, and, granted the premise that 1159 cm.^{-1} (A_1') is the highest skeletal frequency, there are rather few alternatives for the lower ones. The specific identifications of the hydrogen deformation frequencies are, of course, more tentative.

The prospects of refining the calculation of the molecular frequencies in a complete calculation turn out to be reasonably good, since closely spaced pairs of skeletal and hydrogen modes of like symmetry are few, so that the values of the interaction constants should not be particularly critical. Conversely, however, the possibility of determining these constants convincingly is reduced. At the same time it is clearly necessary to modify the force field around the tertiary carbon atoms; our procedure of using angle constants derived from Larnaudie's figures for C-CH₂-C is distinctly crude. Further changes may be entailed by the circumstance that Larnaudie assumed the chair conformation for cyclohexane; the cyclohexane rings in bicyclo-octane are locked in the boat form. Concerning the conformation of bicyclo-octane itself we can only say that the twisting, if any, about the 3-fold axis must be slight; the estimates of the torsional force constant (it emerges as a small difference between large numbers) and thus of the A_1'' frequency are altogether too uncertain to be adduced as evidence in this connection. Thermochemical studies¹³ have yielded a similarly equivocal conclusion.

APPENDIX: Calculation of the skeletal frequencies

The following treatment assumes a simplified model in which the CH and CH₂ groups are treated as mass points, centred at the equilibrium positions of the carbon nuclei. As explained in the discussion of the spectral assignments, the D_{3h} molecular configuration is assumed; the CCC angles are all tetrahedral and the CC bonds all have their usual lengths (1.54 \AA).

Internal displacement co-ordinates are selected as follows (cf. Fig. 2); bond stretches (r , s), angle deformations (α , β), and torsions (τ) of the CCCC chains terminating at the tertiary carbon atoms. The torsions are positive for displacement in the direction of the arrows in Fig. 2(b). It happens that one of the sets of angle deformations, α or β , is redundant; nevertheless, they are included in the algebra in order that elastic constants derived from open-chain alkanes may be transferred to the bicyclic molecule. The set of internal co-ordinates thus defined forms a basis for a reducible representation of the D_{3h} group with components $4A_1' + A_1'' + 3A_2'' + E' + E''$; one redundancy is located in each of A_1' , A_2'' , E' and E'' .

The following symmetry co-ordinates are defined:

$$\begin{aligned}
 A_1': & \quad 3^{-\frac{1}{2}} (s_1 + s_3 + s_5) \\
 & \quad 6^{-\frac{1}{2}} (r_1 + r_2 + r_3 + r_4 + r_5 + r_6) \\
 & \quad 6^{-\frac{1}{2}} (\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 + \alpha_5 + \alpha_6) \\
 A_1'': & \quad 3^{-\frac{1}{2}} (\tau_1 + \tau_2 + \tau_3) \\
 A_2'': & \quad 6^{-\frac{1}{2}} (r_1 - r_2 + r_3 - r_4 + r_5 - r_6) \\
 & \quad 6^{-\frac{1}{2}} (\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6) \\
 E': & \quad 6^{-\frac{1}{2}} (2s_1 - s_3 - s_5) \\
 & \quad 12^{-\frac{1}{2}} (2r_1 + 2r_2 - r_3 - r_4 - r_5 - r_6) \\
 & \quad 12^{-\frac{1}{2}} (-\alpha_1 - \alpha_2 + 2\alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6) \\
 E'': & \quad 12^{-\frac{1}{2}} (2r_1 - 2r_2 - r_3 + r_4 - r_5 + r_6) \\
 & \quad 12^{-\frac{1}{2}} (-\alpha_1 + \alpha_2 + 2\alpha_3 - 2\alpha_4 - \alpha_5 + \alpha_6) \\
 & \quad 2^{-\frac{1}{2}} (\tau_3 - \tau_5)
 \end{aligned} \tag{1}$$

Only one set of symmetry co-ordinates is specified for the degenerate species E' , E'' . Symmetry co-ordinates in β can be obtained by substituting β for r in the four symmetry co-ordinates which involve r .

Wilson's FG matrix method¹⁴ is then followed. The factored G matrices, in terms of

¹² Ramsay and Sutherland, *Proc. Roy. Soc.*, 1947, *A*, **190**, 245.

¹³ Turner, Meador, and Winkler, *J. Amer. Chem. Soc.*, 1957, **79**, 4116.

¹⁴ Wilson, Decius, and Cross, "Molecular Vibrations," McGraw-Hill, New York, 1955.

TABLE 4. *G* matrices of symmetry co-ordinates for the skeletal vibrations of bicyclo[2,2,2]octane.

| Species | <i>G</i> matrix | | |
|-----------|-----------------|--|---|
| $A_{1'}$ | s | $\begin{bmatrix} 2\mu \\ -2\frac{1}{2}\mu/3 \\ 4\mu/3 \end{bmatrix}$ | $\begin{bmatrix} \mu + \mu'/3 \\ -2\cdot 2\frac{1}{2}\rho\mu'/3 \\ \rho^2(\mu + 8\mu'/3) \end{bmatrix}$ |
| $A_{1''}$ | τ | $[3\cdot 6\frac{1}{2}\rho^2\mu'/2]$ | |
| $A_{2''}$ | r | $\begin{bmatrix} \mu + \mu'/3 \\ -2\cdot 2\frac{1}{2}\rho\mu'/3 \end{bmatrix}$ | $\rho^2(\mu + 8\mu'/3)$ |
| E' | s | $\begin{bmatrix} 2\mu \\ -2\frac{1}{2}\mu/3 \\ -2\rho\mu/3 \end{bmatrix}$ | $\begin{bmatrix} \mu + 4\mu'/3 \\ 4\cdot 2\frac{1}{2}\rho\mu'/3 \\ \rho^2(5\mu/2 + 8\mu'/3) \end{bmatrix}$ |
| E'' | r | $\begin{bmatrix} \mu + 4\mu'/3 \\ 4\cdot 2\frac{1}{2}\rho\mu'/3 \\ -3\cdot 2\frac{1}{2}\rho\mu'/3 \end{bmatrix}$ | $\begin{bmatrix} \rho^2(5\mu/2 + 8\mu'/3) \\ -3\rho^2(5\mu/4 + \mu') \\ \rho^2(25\mu/4 + 27\mu'/8) \end{bmatrix}$ |

Matrices are symmetric; upper off-diagonal terms omitted.

symmetry co-ordinates, are given in Table 4 (μ , μ' = reciprocal masses of CH_2 , CH ; ρ = reciprocal of CC bond length). In this Table the elements corresponding to symmetry co-ordinates in the angles β are not given, since they may be deduced from the following redundancy conditions [in which the letters stand for the *symmetry* co-ordinates, as defined by eqns. (1), of the indicated symmetry species]:

$$\begin{aligned}
 A_{1'}: & \quad \beta + \alpha = 0 \\
 A_{2''}: & \quad 3\beta + 4\cdot 2\frac{1}{2}\rho r + 5\alpha = 0 \\
 E': & \quad 4\beta + 3\rho s + 2\frac{1}{2}\rho r = 0 \\
 E'': & \quad 3\beta + 4\cdot 2\frac{1}{2}\rho r - 10\alpha - 6\tau = 0
 \end{aligned} \tag{2}$$

The complete quadratic potential in terms of all the chosen co-ordinates (including the β 's) is then written down. This contains 37 constants of which only 22 are independent. If the constants in this redundant force field are to be identified with the corresponding constants of

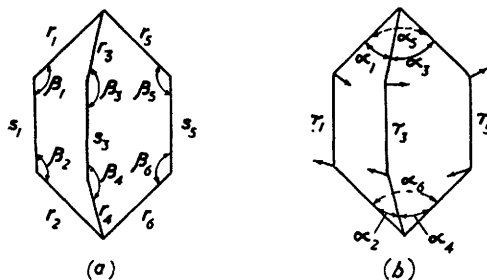


FIG. 2. Internal valency co-ordinates for displacements of the carbon skeleton of bicyclo[2,2,2]octane.

less highly connected molecules, without adding linear terms, it is necessary that in the equilibrium configuration of the molecule as a whole each internal co-ordinate should have the same value as it would have were the cyclic constraints removed: that is, the molecule should be unstrained. Apart from the possible effects of methylene repulsions, this condition appears to be satisfied in bicyclo-octane.

The redundancy equations (2) were then used to eliminate the β co-ordinates. The resulting *F* matrices, though straightforwardly derived, are rather lengthy to specify and will therefore not be reproduced here. The secular equations were then solved by using *F* matrices constructed from various sets of internal-co-ordinate force constants.

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