

# Interactions Between *cis*-Ethylene Ligands Studied by Inelastic Neutron Scattering

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The inelastic neutron scattering spectra of  $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ ,  $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)\text{SO}_2$  and  $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$  have been measured and the torsional vibrations of their ethylene groups have been assigned. In the diethylene compounds in-phase and out-of-phase torsions have been observed and for  $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$  their frequencies are  $112 \pm 5$  and  $226 \pm 5 \text{ cm}^{-1}$ . A model has been proposed for the interaction between the ethylene groups and the experimentally observed frequencies have been expressed in terms of constants derived from this model.

To obtain further information about the torsion potentials of ethylene molecules bound to metal atoms we have studied the vibrations of the ethylene groups in  $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ ,  $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$  and  $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)\text{SO}_2$  with inelastic neutron scattering (i.n.s.). These data will be of value in the interpretation of the spectra of adsorbed molecules. In the first two compounds the ethylene groups are bound in a *cis* configuration to their metal atoms and we have been able to observe the interactions between the groups through the splittings between their in-phase and out-of-phase torsions. These interactions have been expressed in terms of constants in the Fourier expansions of the potential energies of the rotating ethylene groups. Confirmation of our interpretation is provided by the spectrum of  $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)\text{SO}_2$ . Ethylene rotation in the two cyclopentadiene compounds has also been studied with n.m.r.<sup>1</sup> and the combination of the i.n.s. and n.m.r. results leads to more detailed information than can be obtained from either method independently.

## EXPERIMENTAL

$[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$  was obtained from Strem Chemicals Inc.,  $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$  was kindly donated by Dr. R. Cramer and  $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)\text{SO}_2$  was prepared as described in the literature.<sup>2</sup> All samples were handled in inert atmospheres and examined as polycrystalline powders. Both cyclopentadiene complexes were sandwiched between 0.05 mm-thick aluminium foil whereas the  $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$  was contained in a thin-walled silica cell.

The neutron spectra were recorded at room temperature, with the 6H long wavelength spectrometer at A.E.R.E. Harwell (U.K.).<sup>3</sup> The sample, an identical sample container and a standard vanadium plate were cycled periodically through the neutron beam during the experiments. The spectra at 9 angles of scatter between 18 and 90° were collected simultaneously. The spectra of the sample containers were subtracted from the sample spectra and using data from the vanadium the results from the different detectors were normalised and the double differential scattering cross-section calculated for each scattering angle.

The amplitude weighted frequency distribution function  $\rho(\omega)$ <sup>4</sup> was estimated by extrapolating results from several angles to zero momentum transfer. Although this procedure

involves a one-phonon approximation the actual positions of the peaks in the raw time-of-flight data correspond very closely to their positions in  $\rho(\omega)$ . This is to be expected since the approximations made in the treatment become good for all one phonon systems as  $K \rightarrow 0$ .<sup>5</sup>  $K$  is the momentum transfer.

The infrared measurements were made using a Beckman-RIIC FS720 Fourier Transform spectrophotometer. Samples were run as Nujol mulls supported on a polythene disc. The Raman measurements we made with a Cary 82 Laser Raman spectrophotometer using a wavelength of 632.8 nm with approximately 10 mW power at the sample.

## RESULTS AND DISCUSSION

### ASSIGNMENT OF SPECTRA

The frequency distributions  $\rho(\omega)$ , of  $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$ ,  $\text{Fe}(\pi\text{-C}_5\text{H}_5)_2$ ,  $\text{Rh}(\text{C}_2\text{H}_4)_2(\pi\text{-C}_5\text{H}_5)$  and  $\text{Rh}(\text{C}_2\text{H}_4)(\text{SO}_2)(\pi\text{-C}_5\text{H}_5)$ , obtained from energy-gain inelastic neutron scattering are shown in fig. 1-4, and the results together with those from the Raman and infrared spectra are summarized in table 1.

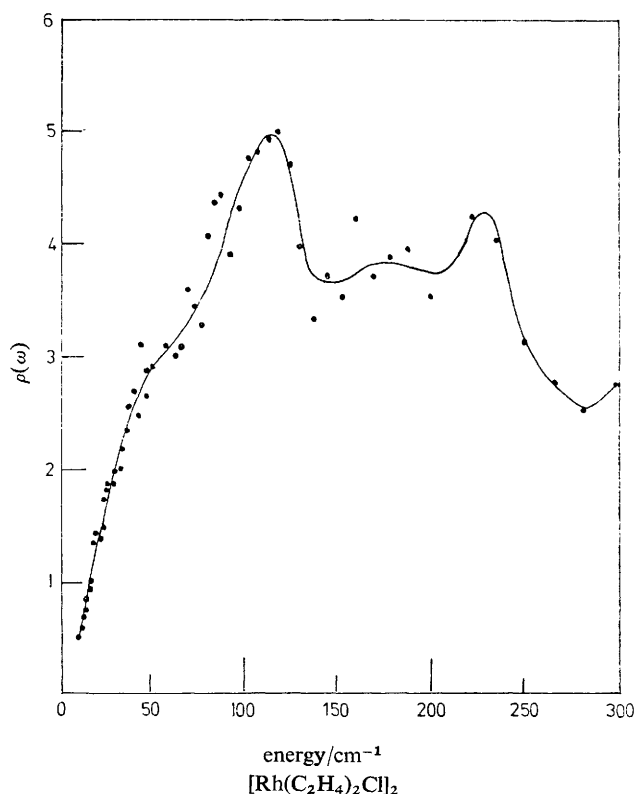
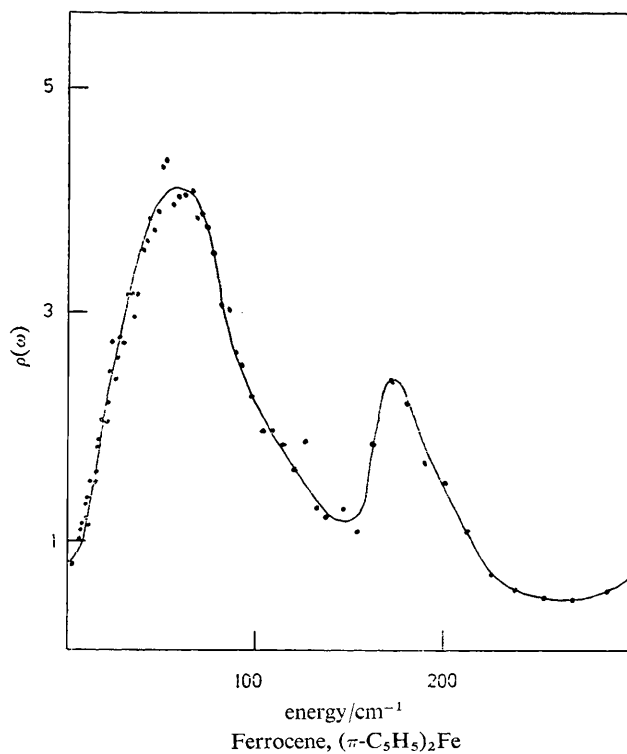


FIG. 1.—Amplitude weighted density of states spectrum of  $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$ .

To a first approximation each of the spectra of the cyclopentadiene compounds is separable into the vibrations of its constituents, i.e., the scattering due to the cyclopentadienyl ring should be separable from that due to the ethylene ligands. Such a separation procedure is not, in general, possible with optical spectra because of the changes in selection rules which may occur as a result of substitution; however, this

FIG. 2.—Amplitude weighted density of states spectrum of  $(\pi\text{-C}_5\text{H}_5)_2\text{Fe}$ .TABLE 1.—SUMMARY OF I.R., RAMAN AND I.N.S. DATA ( $\text{cm}^{-1}$ )

$(\pi\text{-C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{H}_4)_2$			$[(\text{C}_2\text{H}_4)_2\text{RhCl}]_2$			$\pi\text{-C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)\text{SO}_2$		$(\pi\text{-C}_5\text{H}_5)_2\text{Fe}$		
i.n.s.	i.r. <sup>a</sup>	Raman	i.n.s.	i.r. <sup>a</sup>	Raman	i.n.s.	i.r. <sup>a</sup>	i.n.s.	i.r. <sup>b</sup>	Raman <sup>a,c</sup>
		30		29	21					
				39	40					48(?)
50		60	50	50	50	52		56		57
					60				60	65
					84				70	73
100			112	118	123				83	82
	140(?)			138		125	124			
				146			141			
165	166	171	160	172	170	175	185(sh)	174	179	
230							197		186	
	242	244	226	220						

<sup>a</sup> At liquid-nitrogen temperature; <sup>b</sup> ref. (7); <sup>c</sup> ref. (22).

separation will be valid for the neutron spectra if there is no coupling between the motions of the  $\text{C}_5\text{H}_5$  ring and the ethylene ligands. It is believed, from a variety of experimental evidence, e.g., n.m.r. work,<sup>6</sup> infrared results,<sup>7</sup> electron diffraction<sup>8</sup> and from a study of the number and type of acetylenylferrocene isomers<sup>9</sup> that the

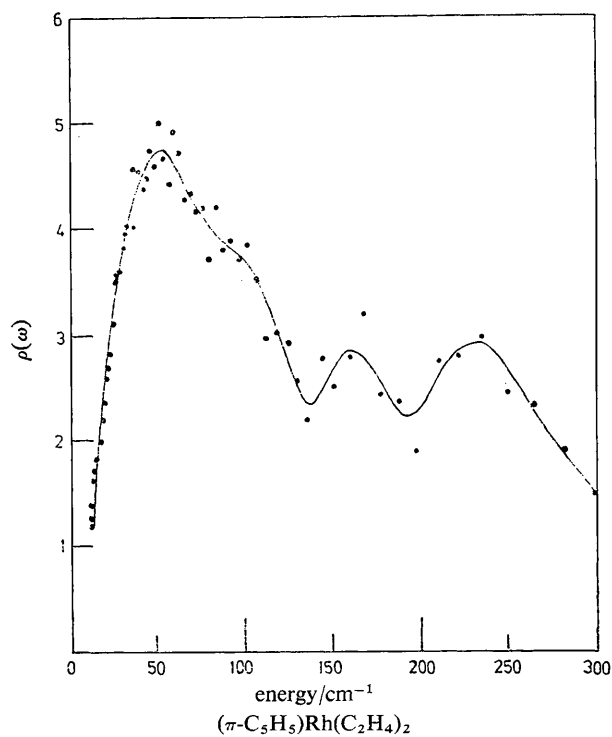


FIG. 3.—Amplitude weighted density of states spectrum of  $(\pi\text{-C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{H}_4)_2$ .

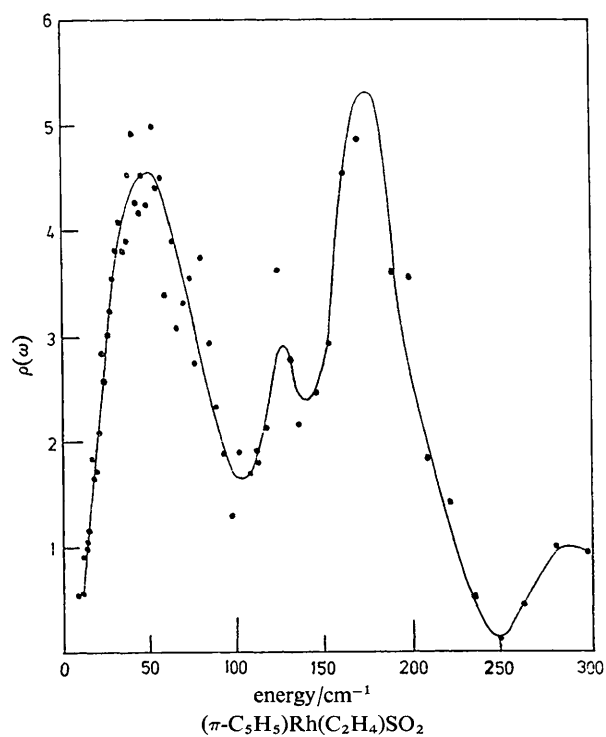


FIG. 4.—Amplitude weighted density of states spectrum of  $(\pi\text{-C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{H}_4)\text{SO}_2$ .

torsional motions of the  $C_5H_5$  rings in  $Fe(\pi-C_5H_5)_2$  are virtually free. We consider that a similar situation obtains in  $\pi-C_5H_5Rh(C_2H_4)_2$  and  $\pi-C_5H_5Rh(C_2H_4)SO_2$ . The n.m.r.<sup>2, 10</sup> results for these compounds show only a single absorption for the protons on the  $C_5H_5$  ring. The separation is further supported by the similarity of the i.n.s. spectra of  $Rh(\pi-C_5H_5)(C_2H_4)_2$  and  $[Rh(C_2H_4)_2Cl]_2$  in the low-frequency region. In the solid state the formal number of electrons at the metal atom in  $[Rh(C_2H_4)_2Cl]_2$  is identical to that in  $Rh(\pi-C_5H_5)(C_2H_4)_2$ <sup>10</sup> because of the extra interactions between metal atoms in neighbouring molecules. Consequently, it is not unexpected that the ethylene vibrations in these two molecules are similar; rather it gives additional confirmation to our assignments. Thus, in our analysis we treat the  $C_5H_5$  ring as a massive freely rotating group. The scattering from the ethylene ligands can be obtained from our results by separating the spectrum of the  $(\pi-C_5H_5)Rh$  group, a good description of which we consider to be provided by ferrocene,  $(\pi-C_5H_5)_2Fe$ .<sup>12</sup>

The i.n.s. spectrum of ferrocene contains bands at  $56 \pm 5$  and  $174 \pm 5$   $cm^{-1}$  in the low energy region. The peak at 174  $cm^{-1}$  corresponds to an i.r. band at 179  $cm^{-1}$  which has been assigned to a ring-metal-ring bending mode.<sup>13</sup> The peak at approximately 50  $cm^{-1}$  in the spectra of the cyclopentadiene compounds we thus assign to a vibration of the  $C_5H_5$  ring by analogy with the  $(\pi-C_5H_5)_2Fe$  spectrum.

By analogy with the spectra of Zeise's salt and related compounds<sup>14</sup> the peak at  $173 \pm 5$   $cm^{-1}$  in the i.n.s. spectrum of the  $SO_2$  compound can be assigned to the ethylene torsion vibration. As predicted from consideration of the moment of inertia and mass of the ethylene group,<sup>14</sup> only weak intensity is seen in the regions 110-130 and 190-200  $cm^{-1}$  where the rock and wag vibrations are expected to occur<sup>15, 16, 17</sup> with intensity approximately  $\frac{1}{3}$  that of the torsion vibration. The peak at  $125 \pm 5$   $cm^{-1}$  is probably the wag and the rock is not resolved from the much stronger torsional peak.

The i.n.s. spectrum of  $[(C_2H_4)_2RhCl]_2$  contains four features. The two most intense bands, at  $112 \pm 5$  and  $226 \pm 5$   $cm^{-1}$ , we assign to the in-phase (i.p.) and the out-of-phase (o.p.) torsions respectively of the ethylene ligands. No assignment which omits i.p. and o.p. torsion vibrations can account for the similar intensities of the peaks in this spectrum. An assignment of one peak to a torsion vibration and another to a particular bending vibration of the ethylene-metal bond would be unacceptable on intensity grounds.

The i.n.s. spectrum of  $Rh(\pi-C_5H_5)(C_2H_4)_2$  also has four bands. The band at 50  $cm^{-1}$  we have already assigned to a vibration of the  $C_5H_5$  ring by comparison with the spectra of ferrocene. The remainder of the spectrum is very similar to that of  $[Rh(C_2H_4)_2Cl]_2$ . Thus, for identical reasons, we assign the bands at 100 and 230  $cm^{-1}$  to i.p. and o.p. torsions of the ethylene groups.

I.r. and Raman spectra (table 1) are not particularly helpful in confirming these assignments. Both diethylene compounds are of  $C_{2v}$  symmetry so that all vibrations are Raman active and only those of  $A_2$  symmetry are i.r. inactive. Thus, we were unable to detect an i.r. band corresponding to the i.p. ( $A_2$ ) torsion in  $Rh(\pi-C_5H_5)(C_2H_4)_2$  as would be expected; however, we were also unable to detect a Raman signal close to this frequency. The o.p. torsion for  $Rh(\pi-C_5H_5)(C_2H_4)_2$  ( $B_1$ ) has corresponding i.r. and Raman bands as expected. The i.p. and o.p. torsions in  $[Rh(C_2H_4)_2Cl]_2$  are of symmetry  $B_1$  and  $A_1$  respectively and we were unable to detect a Raman signal corresponding to the o.p. torsion.

$(\pi-C_5H_5)Rh(C_2H_4)SO_2$  is of  $C_s$  symmetry and so all modes should be i.r. and Raman active. We were unable to obtain the Raman spectrum of this complex.

CALCULATION OF BARRIERS FROM THE TORSIONAL FREQUENCIES.  
POTENTIAL ENERGY CALCULATIONS

We now calculate how the potential energy of a pair of *cis*-ethylene ligands can be expected to vary during in-phase and out-of-phase rotation. We also obtain simple formulae for these potential functions which can then be used to interpret the assignments we have made.

If  $\alpha_1$  and  $\alpha_2$  are the clockwise rotational angular displacements of the two ethylene groups about the axes joining their midpoints to the metal atom, then the variation of the potential energy of the ethylene ligands, on rotation, may be written as

$$V_{\text{total}}(\alpha_1, \alpha_2) = V(\alpha_1, \alpha_2) + V_T(\alpha_1) + V_T(\alpha_2), \quad (1)$$

where  $\alpha_1 = \alpha_2 = 0$  in the ground vibrational state conformation.  $V(\alpha_1, \alpha_2)$  is the potential energy variation due to the *cis*-ethylene interactions and  $V_T(\alpha_1)$  and  $V_T(\alpha_2)$  are the potential energy variations due to interactions with the remainder of the molecule.

$V(\alpha_1, \alpha_2)$ :

$V(\alpha_1, \alpha_2)$  is, in general, a complex function of  $\alpha_1$  and  $\alpha_2$  but for the in-phase ( $\alpha_1 = \alpha_2$ ) and out-of-phase ( $\alpha_1 = -\alpha_2$ ) motions the potential energy variations may be expressed as

$$V(\alpha, -\alpha) = \sum_{n=1}^{\infty} V_{2n}(1 - \cos 2n\alpha), \quad (2)$$

$$V(\alpha, \alpha) = \sum_{n=1}^{\infty} V_{2n}(1 - \cos 2n\alpha) + \sum_{n=1}^{\infty} \frac{1}{2} V'_{4n}(1 - \cos 4n\alpha). \quad (3)$$

For a discussion of this result see the Appendix.

We have numerically calculated values of  $V(\alpha, \alpha)$  and  $V(\alpha, -\alpha)$  for a *cis*-diethylene complex to decide where these series may be truncated. The calculations used the function,

$$V(R) = 11.094 \times 10^3 \exp(-3.74R) - 114.1R^{-6} \text{ kJ mol}^{-1}$$

due to Williams,<sup>18</sup> where  $R$  is the hydrogen-hydrogen separation in Å.

The intramolecular interaction potentials between hydrogens on the ethylenes and those on the  $\text{C}_5\text{H}_5$  ring are approximately 1 % of the potentials between hydrogens on the different ethylene ligands. The structural parameters used in this calculation were those determined for  $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)(\text{C}_2\text{F}_4)$ <sup>19</sup> and the angle between the three-membered ethylene-metal ring was taken from this structure, but with less justification, as  $95^\circ$ . Plots of the calculated values of  $V(\alpha, \alpha)$  and  $V(\alpha, -\alpha)$  are shown in fig. 5. To determine the importance and size of the individual coefficients eqn (2) and (3) were fitted to these curves by the method of least squares. Because the exact geometry of the  $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$  molecule is not known and the higher Fourier coefficients were found to be small and interdependent, it was decided that the simple potential functions shown below, which correctly reproduce the essential details of the calculated curves, would be used for further data analysis.

$$V(\alpha, -\alpha) = V_2(1 - \cos 2\alpha) + V_4(1 - \cos 4\alpha), \quad (4)$$

$$V(\alpha, \alpha) = V_2(1 - \cos 2\alpha) + V_4(1 - \cos 4\alpha) + \frac{1}{2} V'_4(1 - \cos 4\alpha) + \frac{1}{2} V'_8(1 - \cos 8\alpha). \quad (5)$$

The best fits of these functions to the calculated curves together with the values obtained for the Fourier coefficients are also shown in fig. 5. Our theory indicates

that the first Fourier coefficients, for the in-phase and out-of-phase motions, will be equal and from fig. 5 this can be seen to be the case.

$V_T(x)$ :

We now find a value for  $V_T(x)$  by using the n.m.r. and i.n.s. data for  $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)\text{SO}_2$  to determine the form of the potential function for rotation of a single ethylene ligand. Using this form to describe the situation for the diethylene complex when only a single ethylene rotation is being observed, as in the n.m.r. experiment, we can use the n.m.r. barrier to obtain  $V_T(x)$ .

We assume that there is negligible steric hindrance to the rotation of the ethylene ligand in  $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)\text{SO}_2$  and that the torsion potential may be expressed as

$$V_{\text{total}}(x) = V_T(x) = \frac{1}{2}V^T(1 - \cos 2x).$$

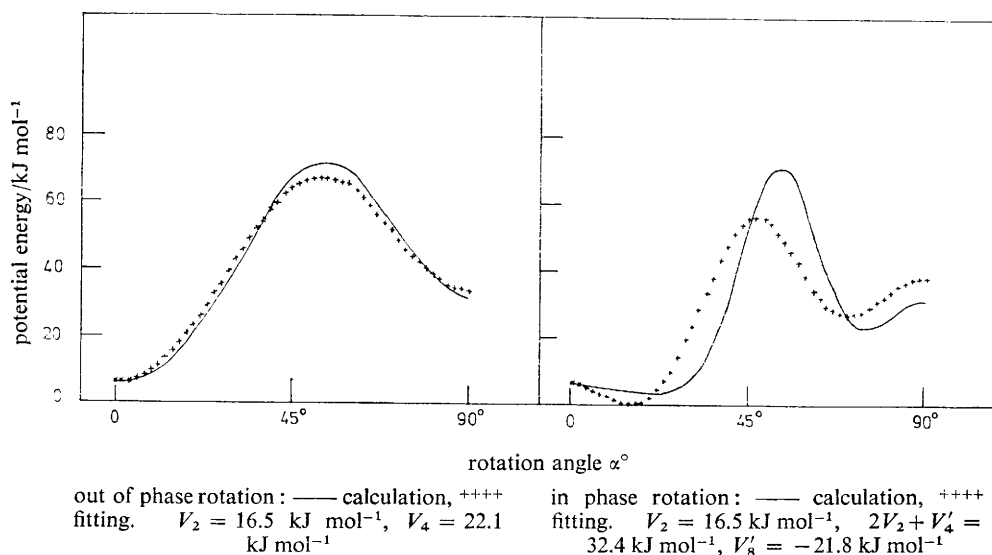


FIG. 5.—Potential energies calculated for *cis*-ethylene ligands, using the function due to Williams, and the best fits to them.

Using the simple harmonic oscillator formula, this simple two-fold potential leads to a value of  $V^T$ , obtained from the neutron data of  $109.3 \pm 6 \text{ kJ mol}^{-1}$  which compares with the n.m.r. value of  $51.1 \text{ kJ mol}^{-1}$ . This discrepancy is expected since work on Zeise's salt<sup>14</sup> showed the necessity of including a four-fold term in the torsion potential in order to account for the increase in  $d_\pi-p_\pi$  bonding after rotation of the ethylene group by  $90^\circ$  from the ground state position. By using an equation of the form

$$V_T(x) = \frac{1}{2}V^T(1 - \cos 2x) + (V^T/2x)(1 - \cos 4x), \quad (6)$$

we can effect agreement between the n.m.r. and i.n.s. data. This leads to a value for  $x$  of approximately  $\frac{7}{2}$  and with this value the n.m.r. barrier to rotation is still numerically approximately equal to  $V^T$ . The four-fold contribution is smaller than that found for Zeise's salt but there is still a very small metastable minimum in  $V_T(x)$  at  $\alpha = 90^\circ$ .

We assume that eqn (6) (with  $x = \frac{7}{2}$ ) may also be applied to the complex  $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$  and that we may use its n.m.r. barrier ( $62.7 \text{ kJ mol}^{-1}$ ) for  $V^T$ .

This treatment neglects the effect of intermolecular interactions in the solid state.

The justification for this is that good agreement between theoretical and experimental values of the barrier in Zeise's salt was found using this approximation.

#### COMPARISON WITH EXPERIMENTAL RESULTS

By substituting eqn (4), (5) and (6) into eqn (1), we obtain analytic expressions for  $V_{\text{total}}(\alpha, \alpha)$  and  $V_{\text{total}}(\alpha, -\alpha)$ . Again, using the harmonic oscillator formula, we obtain the following expressions for the energy separations of the 0-1 torsional transitions of the ethylene groups :

$$\omega_{\text{o.p.}} = \frac{1}{2\pi I_r^{\frac{1}{2}}} (2V_2 + 8V_4 + 4.3V^T)^{\frac{1}{2}} \text{ for the out-of-phase rotation,} \quad (7)$$

$$\omega_{\text{i.p.}} = \frac{1}{2\pi I_r^{\frac{1}{2}}} (2V_2 + 8V_4 + 4V'_4 + 16V'_8 + 4.3V^T)^{\frac{1}{2}} \text{ for the in-phase rotation,} \quad (8)$$

where  $I_r$  is the reduced moment of inertia of an ethylene ligand. Substituting for the experimental values of  $\omega_{\text{o.p.}}$  and  $\omega_{\text{i.p.}}$  for  $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$  and using the value of  $62.7 \text{ kJ mol}^{-1}$  for  $V^T$  enables us to calculate values for  $V_2 + 4V_4$  and  $V'_4 + 4V'_8$  these being  $58.3 \pm 7.5$  and  $-78.2 \pm 6 \text{ kJ mol}^{-1}$  respectively. These values can be compared with those obtained by the curve fitting to the numerical calculation of 105 and  $-98.8 \text{ kJ mol}^{-1}$  respectively.

As there is no simple method for the accurate determination of energy barriers of processes leading to the collapse of a  $AA'BB'X$  spin system to an  $A_4X$  system, approximate methods were employed in the determination of the barriers to rotation by n.m.r. The values we have quoted were calculated from computer line-shape analysis by a method which gives predicted line shapes which are in good agreement with the experimental data. The value for  $\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$  has also been calculated<sup>20</sup> ( $65.9 \text{ kJ mol}^{-1}$ ) by using an approximate equation which is subject to the limitations outlined by Raban *et al.*<sup>21</sup> This value is in reasonable agreement with the value calculated from the line shape analysis ( $62.7 \text{ kJ mol}^{-1}$ ).

Eqn (7) and (8) are sensitive to the experimental values of the n.m.r. barriers. For instance, if the value of  $51.1 \text{ kJ mol}^{-1}$  for the  $(\pi\text{-C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{H}_4)\text{SO}_2$  compound were too low by more than 7 % then the value of  $x$ , in eqn (6), would change and the metastable minimum at  $\alpha = 90^\circ$  would disappear. However, the n.m.r. barrier would still be approximately equal to  $V^T$ . The major change would be a reduction in the coefficient of  $V^T$  in eqn (7) and (8). This would not alter the value of  $V'_4 + 4V'_8$  but it would lead to an increase in  $V_2 + 4V_4$ .

The "splitting interaction"  $-78.2 \text{ kJ mol}^{-1}$ , which is determined straightforwardly from the difference in energy between the in-phase and out-of-phase torsion vibrations, agrees more favourably with the calculations than the other term which requires more assumptions in its determination.

Errors in the assumptions behind the above calculations are likely to arise from at least three sources : (i) a distortion of the ethylene ligand during rotation, (ii) the competition between the two ethylene groups for the  $d_{xy}$  electrons, of the metal atom, when  $\alpha_1 = \alpha_2 = 90^\circ$ , and (iii) the intermolecular interactions mentioned earlier.

The bridging of the torsion frequency of the  $\text{SO}_2$  compound by those of the diethylene complex can be seen to be caused by the opposing effects of  $V_2 + 4V_4$  on the out-of-phase torsion and  $V'_4 + 4V'_8$  on the in-phase torsion.

One of us (J. H.) thanks the A.E.R.E. (Harwell) for the provision of a research studentship.



## APPENDIX

$V_{\text{total}}(\alpha_1, \alpha_2)$  may be written

$$V_{\text{total}}(\alpha_1, \alpha_2) = f_1(\alpha_1) + f_2(\alpha_2) + f_{1,2}(\alpha_1 \pm \alpha_2).$$

For the molecules under consideration molecular symmetry requires that

$$V_{\text{total}}(\alpha_1, \alpha_2) = V_{\text{total}}(-\alpha_1, -\alpha_2)$$

$$V_{\text{total}}(\alpha_1, \alpha_2) = V_{\text{total}}(\alpha_1 + \pi, \alpha_2)$$

$$V_{\text{total}}(\alpha_1, \alpha_2) = V_{\text{total}}(\alpha_1, \alpha_2 + \pi)$$

$$V_{\text{total}}(\alpha_1, \alpha_2) = V_{\text{total}}(\alpha_1 + \pi, \alpha_2 + \pi)$$

$$f_1(\alpha_1) = f_2(\alpha_1)$$

$$f_1(\alpha_1) = f_1(-\alpha_1)$$

$$f_{1,2}(\alpha_1 \pm \alpha_2) = f_{1,2}(-\{\alpha_1 \pm \alpha_2\})$$

$$f_1(\alpha) = f_1(\pi + \alpha).$$

We may therefore express  $f_1$  and  $f_{1,2}$  as Fourier series

$$f_1(\alpha_1) = f_2(\alpha_1) = \sum_{n=1}^{\infty} \frac{1}{2} \bar{V}_{2n} (1 - \cos 2n\alpha_1), \quad (\text{A1})$$

$$f_{1,2}(\alpha_1 \pm \alpha_2) = \sum_{n=1}^{\infty} \frac{1}{2} V'_{4n} (1 - \cos 2n(\alpha_1 \pm \alpha_2)), \quad (\text{A2})$$

where the factor 2 in the numerator of eqn (A2) is derived using  $V_{\text{total}}(\frac{1}{2}\pi, \frac{1}{2}\pi) = V_{\text{total}}(\frac{1}{2}\pi, -\frac{1}{2}\pi)$ . Considering only the case where  $f_{1,2}$  is expressed as the sum of  $\alpha_1$  and  $\alpha_2$  and applying the simple harmonic oscillator approximation we obtain

$$V_{\text{total}}(\alpha_1, \alpha_2) = \sum_{n=1}^{\infty} \{(n^2 \bar{V}_{2n} + n^2 V'_{4n}) \alpha_1^2 + (n^2 \bar{V}_{2n} + n^2 V'_{4n}) \alpha_2^2 + 2n^2 V'_{4n} \alpha_1 \alpha_2\}.$$

Writing

$$k = 2 \sum_{n=1}^{\infty} (n^2 \bar{V}_{2n} + n^2 V'_{4n}),$$

$$k_{1,2} = \sum_{n=1}^{\infty} 2n^2 V'_{4n},$$

then the potential energy is

$$V_{\text{total}}(\alpha_1, \alpha_2) = \frac{1}{2} k \alpha_1^2 + \frac{1}{2} k \alpha_2^2 + k_{1,2} \alpha_1 \alpha_2.$$

Writing the kinetic energy as  $\frac{1}{2} I_r \dot{\alpha}_1^2 + \frac{1}{2} I_r \dot{\alpha}_2^2$ , where  $I_r$  is the reduced moment of inertia of a single ethylene ligand, and solving Lagrange's equations for the system we obtain

$$\omega^2 = \frac{1}{4\pi^2} \left( \frac{k \pm k_{1,2}}{I_r} \right).$$

Hence

$$\omega_1 = \frac{1}{2\pi} \left( \frac{k + k_{1,2}}{I_r} \right)^{\frac{1}{2}} = \frac{1}{2\pi} \left( \frac{\sum_{n=1}^{\infty} (2n^2 \bar{V}_{2n} + 4n^2 V'_{4n})}{I_r} \right)^{\frac{1}{2}},$$

$$\omega_2 = \frac{1}{2\pi} \left( \frac{k - k_{1,2}}{I_r} \right)^{\frac{1}{2}} = \frac{1}{2\pi} \left( \frac{\sum_{n=1}^{\infty} 2n^2 \bar{V}_{2n}}{I_r} \right)^{\frac{1}{2}},$$

and

$$\omega_1^2 - \omega_2^2 = \frac{1}{4\pi^2} \left( \frac{\sum_{n=1}^{\infty} 4n^2 V'_{4n}}{I_r} \right).$$

The solution  $\omega_1$  corresponds to motion where  $\alpha_1 = \alpha_2$ , and  $\omega_2$  to motion where  $\alpha_1 = -\alpha_2$ . We expect the in-phase motion ( $\alpha_1 = \alpha_2$ ) to have the lower frequency. Thus,

$$V_{\text{total}}(\alpha, \alpha) = \sum_{n=1}^{\infty} \bar{V}_{2n}(1 - \cos 2n\alpha) + \sum_{n=1}^{\infty} \frac{1}{2} V'_{4n}(1 - \cos 4n\alpha) \text{ for in-phase motion,}$$

$$V_{\text{total}}(\alpha, -\alpha) = \sum_{n=1}^{\infty} \bar{V}_{2n}(1 - \cos 2n\alpha) \text{ for out-of-phase motion.}$$

$V_{\text{total}}(\alpha_1, \alpha_2)$  can be rewritten as the sum of the torsional interaction of the ethylene groups with the rest of the molecule  $V_T(\alpha)$  and the "non-bonding" interactions between the ethylene groups  $V(\alpha_1, \alpha_2)$ .

Hence

$$V_{\text{total}}(\alpha_1, \alpha_2) = V(\alpha_1, \alpha_2) + V_T(\alpha_1) + V_T(\alpha_2),$$

where

$$V_T(\alpha_i) = \sum_{n=1}^{\infty} \frac{1}{2} V_{2n}^T(1 - \cos 2n\alpha_i), \quad i = 1 \text{ or } 2,$$

$$V(\alpha_1, \alpha_2) = \sum_{n=1}^{\infty} \frac{1}{2} V_{2n}(1 - \cos 2n\alpha_1) + \sum_{n=1}^{\infty} \frac{1}{2} V_{2n}(1 - \cos 2\alpha_2) + \sum_{n=1}^{\infty} \frac{1}{2} V'_{4n}(1 - \cos 2n(\alpha_1 + \alpha_2)),$$

and

$$V_{2n} = \bar{V}_{2n} - V_{2n}^T.$$

Thus,

$$V(\alpha, \alpha) = \sum_{n=1}^{\infty} V_{2n}(1 - \cos 2n\alpha) + \sum_{n=1}^{\infty} \frac{1}{2} V'_{4n}(1 - \cos 4n\alpha)$$

and

$$V(\alpha, -\alpha) = \sum_{n=1}^{\infty} V_{2n}(1 - \cos 2n\alpha).$$

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