Structural Investigation of the η-Allyl Group in (η-Allyl)tetracarbonylrhenium by Nematic-phase Nuclear Magnetic Resonance Spectroscopy

By **Ian R. Beattie, James W. Emsley,*** **John C. Lindon,** and **Raymond M. Sabine,** Chemistry Department, University of Southampton, Southampton SO9 5NH

The ^{1}H n.m.r. spectrum of (η-allyl)tetracarbonylrhenium dissolved in a nematic phase has been obtained and analysed. Dipolar coupling constants obtained have been used to investigate the structure of the allyl ligand, and it is concluded that the protons do not all lie in one plane. The effect of averaging dipolar couplings over vibrations has been investigated with the aid of a normal-co-ordinate analysis of the vibrations of the allyl ligand.

IN appropriate cases an analysis of the n.m.r. spectrum of a molecule dissolved in an anisotropic medium, such as a nematic liquid-crystal phase, can yield dipolar coupling constants which in turn give structural information.[1] Examples studied so far include such organometallic species as η-cyclopentadienyl compounds,[2-5] tricarbonyl(η-cyclobutadiene)iron,[6,7] [Fe(CO)$_3${CH(CH$_2$)$_3$}],[8] methylmercury halides,[9] and metal

---

[1] P. Diehl and C. L. Khetrepal, 'NMR Basic Principles and Progress,' 1969, vol. 1, p. 1.

[2] C. L. Khetrepal, A. C. Kunwar, and C. R. Kanekar, *Chem. Phys. Letters*, 1971, **9**, 437.

[3] J. C. Lindon and B. P. Dailey, *Mol. Phys.*, 1971, **22**, 465.

[4] A. D. Buckingham, D. Bailey, M. C. McIvor, and A. J. Rest, *Mol. Phys.*, 1973, **25**, 479.

[5] I. R. Beattie, J. W. Emsley, and R. M. Sabine, *J.C.S. Faraday II*, 1974, 1356.

[6] C. S. Yannoni, G. P. Ceasar, and B. P. Dailey, *J. Amer. Chem. Soc.*, 1967, **89**, 2833.

[7] D. Bailey, A. D. Buckingham, and A. J. Rest, *Mol. Phys.*, 1973, **26**, 233.

[8] A. D. Buckingham, A. J. Rest, and J. P. Yesinowski, *Mol. Phys.*, 1973, **25**, 1457.

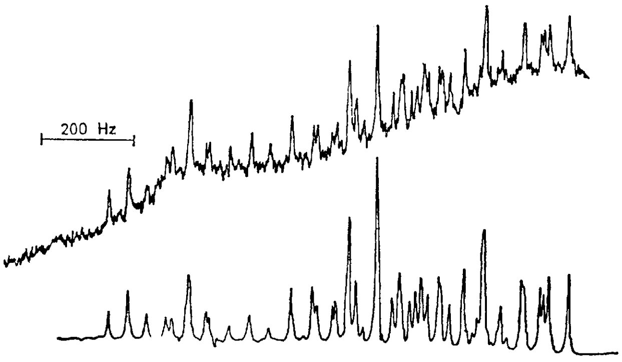
[9] C. L. Khetrepal and A. Saupe, *Mol. Crystals*, 1973, **19**, 195.

hydrides.[10] In some of these studies new structural information has been revealed. We present here details of a study by this technique of (η-allyl)tetracarbonylrhenium, $[Re(CO)_4(C_3H_5)]$. Other η-allyl compounds have been examined but the spectra proved either difficult to obtain or deceptively simple.

The η-allyl compounds have been investigated by X-ray diffraction, but as they contain heavy atoms it has not been possible to locate hydrogen co-ordinates accurately. Usually the allyl group has been assumed to be completely planar;[11-13] however, in the case of 2-methylallyl compounds [14,15] the methyl carbon is not in the plane of the three allyl carbon atoms. The aim of this study has been to see if the n.m.r. spectrum of an oriented sample can reveal any information on the planarity of the allyl group.

EXPERIMENTAL

The sample of (η-allyl)tetracarbonylrhenium was kindly provided by Dr. P. J. Stamper. It was dissolved in the nematic phase of N-(p-ethoxybenzylidene)-p-n-butylaniline (EBBA) to give a concentration of *ca.* 20 mol %. The ^1H n.m.r. spectrum was obtained on a Varian 220 MHz spectrometer under the auspices of the S.R.C. The Figure shows the spectrum together with a computer simulation. Spectra of isotropic-phase samples were obtained on a HA 100 spectrometer.



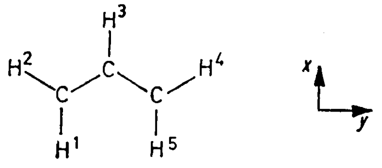
^1H N.m.r. spectrum at 220 MHz of $[Re(CO)_4(C_3H_5)]$ dissolved in EBBA

Analysis of Spectra.—The isotropic-phase spectra are those of a deceptively simple AA′XX′M spin system, from which we obtained directly $|J_{2,3}|$ 7·1, $|J_{1,3}|$ 12·4, and $|J_{1,2} + J_{1,4}|$ 2·8 Hz. The spectrum is consistent with $J_{1,5} = J_{2,4} = 0$ Hz. Double-resonance experiments of the 'spin-tickling' variety established the sign of $(J_{1,2} + J_{1,4})$ as opposite to both $J_{1,3}$ and $J_{2,3}$. Vicinal H–H couplings are usually positive,[16] hence $(J_{1,2} + J_{1,4})$ −2·8 Hz. The collapsed nature of the spectrum means that $|J_{1,2} - J_{1,4}|$ must be near zero, and from the width of the central transition in each part of the aa′xx′ sub-spectra a maximum of 0·6 Hz can be assigned to this difference of coupling constants. Thus $J_{1,2}$ and $J_{1,4}$ can each be equated to $-1·4 \pm 0·3$ Hz.

The spectrum of a sample in EBBA was analysed by keeping the J_{ij} values fixed. A total of 44 transitions was assigned in the iterative part of the analysis, and different signs of D_{ij} and J_{ij} were tried. The set of D_{ij} values given in Table 1 were found to give a significantly better root-mean-square error (1·36 Hz) than any other sign combination.

TABLE 1

N.m.r. parameters obtained from the analysis of $[Re(CO)_4(C_3H_5)]$ dissolved in $CDCl_3$ and in the nematogen EBBA



i,j	J_{ij}/Hz	D_{ij}/Hz
1,2	$-1·4 \pm 0·43$	$105·1 \pm 0·4$
1,3	$12·4 \pm 0·05$	$27·6 \pm 0·3$
1,4	$-1·4 \pm 0·63$	$34·6 \pm 0·4$
1,5	$0·0 \pm 0·05$	$120·5 \pm 0·4$
2,3	$7·1 \pm 0·05$	$125·3 \pm 0·3$
2,4	$0·0 \pm 0·05$	$31·3 \pm 0·4$

δ_{12}/p.p.m. = −1·00 (isotropic) −1·136 (nematic)
δ_{13}/p.p.m. = −2·830 (isotropic) −2·830 (nematic)

RESULTS AND DISCUSSION

The dipolar coupling constants are related to the proton positions through relation (1) provided that the molecule

$$D_{ij} = \frac{-60\,033·5}{r_{ij}{}^3}[S_{zz}(3\cos{}^2\theta_{ijz} - 1) + (S_{xx} - S_{yy})(\cos{}^2\theta_{ijx} - \cos{}^2\theta_{ijy}) + 2S_{xz}\cos\theta_{ijx}\cos\theta_{ijz}] \quad (1)$$

possesses at least one plane of symmetry (the xz plane) and the axis system is as shown in Table 1. The angles $\theta_{ij\alpha}$ are those made by the vector r_{ij} with the α molecule-fixed axes. The terms $S_{\alpha\beta}$ are elements of the ordering matrix (1). For a planar allyl group the term involving S_{xz} is zero and the unknown quantities in equation (1) are the two independent S elements and four proton co-ordinates. However, at least one value of r_{ij} must be specified as equation (1) can yield only relative values of $S_{\alpha\beta}$ and nuclear co-ordinates. Thus there are five unknown quantities for a planar allyl and six observed D_{ij} values, and a least-squares optimisation routine is used to obtain values in best agreement with experiment. From X-ray investigations on the η-allyl compounds, r_{C-C} is *ca.* 1·4 Å. With $\widehat{CCH}$ angles of 120° this yields r_{23} as 2·5 Å; hence this was chosen as the fixed r_{ij} value.

Most of the structure determinations from values of dipolar coupling constants have neglected the effects of vibrational motion. By making this simplifying assumption for $[Re(CO)_4(C_3H_5)]$ we obtained the ordering parameters $S_{\alpha\beta}$ and differences (ΔD_{ij}) between observed and calculated dipolar coupling constants shown in Table 4. It is seen that the ΔD_{ij} values are large and hence the calculation does not support a completely

---

[10] A. D. Buckingham, Y. P. Yesinowski, A. J. Canty, and A. J. Rest, *J. Amer. Chem. Soc.*, 1973, **95**, 2732; D. Bailey, A. D. Buckingham, M. C. McIvor, and A. J. Rest, *J. Organometallic Chem.*, 1973, **61**, 311; Y. P. Yesinowski and D. Bailey, *ibid.*, 1974, **65**, C27.

[11] J. M. Rowe, *Proc. Chem. Soc.*, 1962, 66.

[12] A. E. Smith, *Acta Cryst.*, 1965, **18**, 331.

[13] W. E. Oberlansli and L. F. Dahl, *J. Organometallic Chem.*, 1965, **3**, 43.

[14] R. Uttech and H. Dietrich, *Z. Krist.*, 1965, **122**, 60.

[15] R. Mason and J. D. Roberts, *J. Amer. Chem. Soc.*, 1959, **81**, 1769.

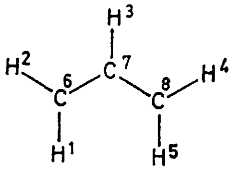
[16] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution NMR Spectroscopy,' Pergamon, 1966, vol. 2.

planar structure. The large residuals could arise because of the neglect of vibrational motion, and we therefore repeated the optimisation with inclusion of vibrational averaging.

To include averaging over molecular vibrations it is necessary to calculate the normal co-ordinates of the molecular vibrations as proposed by Lucas.[17] The vibrational spectrum of the rhenium compound has not been reported, but those of the related molecules $[Mn(CO)_4(C_3H_5)]$ and $[Co(CO)_3(C_3H_5)]$ have been studied.[18-20] We carried out a normal-co-ordinate analysis of the η-allyl group as an isolated molecular fragment at the level of the harmonic-oscillator approximation. The calculation procedure is that described by Beattie *et al.*[21] and internal co-ordinates and valence force field are given in Table 2. In Table 3 we compare the calculated frequencies with those observed for the allyl group in the manganese and cobalt compounds. It is apparent that the ligand vibrations are not strongly influenced by the rest of the molecule, so that we can use the normal co-ordinates calculated to average dipolar couplings in the η-allylrhenium compounds. The descriptions of the vibrations in Table 3 are based on the potential-energy distributions. The optimisation procedure, including vibrational averaging, gives the results shown in the third column of Table 4. It is seen that vibrational averaging has only a small effect on the residuals. Hence we conclude that the η-allyl group cannot be planar.

TABLE 2

Internal co-ordinates and force constants for the η-allyl group



Co-ordinate [a]	Force constant (diagonal elements)/ mdyn Å rad^{-2}
r_{67}, r_{78}	6·121 [b]
r_{16}, r_{26}, r_{48}, r_{58}, r_{37}	4·880 [b]
α_{167}, α_{587}, α_{162}, α_{485}	0·300
α_{267}, α_{784}	0·400
α_{673}, α_{873}	0·626
α_{678}	1·400
γ_{1627}, γ_{5874}	0·032
γ_{2617}, γ_{4857}	0·009
γ_{3768}	0·050
γ_{6738}, γ_{8736}	0·145
ϕ_{2673}, ϕ_{4873}	0·054
ϕ_{1673}, ϕ_{5873}	0·032
ϕ_{1678}, ϕ_{5876}	0·302
ϕ_{2678}, ϕ_{4876}	0·355
	Force constant (off-diagonal)/ mdyn rad^{-1}
r_{67}, r_{78}	0·300 [b]
$r_{67}\alpha_{167}$, $r_{78}\alpha_{587}$	0·300
$r_{67}\alpha_{162}$, $r_{78}\alpha_{485}$	0·477
$r_{67}\alpha_{267}$, $r_{78}\alpha_{487}$	0·300
$r_{67}\alpha_{678}$, $r_{78}\alpha_{678}$	0·400
$r_{67}\alpha_{673}$, $r_{78}\alpha_{873}$	0·600

[a] γ_{ijkl} Is the angle between r_{ij} and the *jkl* plane; ϕ_{ijkl} is the torsional co-ordinate and represents the angle between the planes *ijk* and *jkl*. [b] In mdyn Å^{-1}; 1 dyn = 10^{-5}N.

TABLE 3

Observed and calculated wavenumbers of the allyl group in metal carbonyl compounds

Symmetry	Wavenumber/cm^{-1} Calc.	$[Mn(CO)_4(C_3H_5)]$	$[Co(CO)_3(C_3H_5)]$	Description
A′	3 053	3 022	3 023	CH str.
	3 000	2 972	2 971	CH str.
	2 937	2 946	2 940	CH str.
	1 433	1 464	1 473	CC str., CCH bend
	1 260	1 215	1 228	CCCH twist
	1 047	1 016	1 020	CC str., CCC bend
	963	1 007	1 020	HCCH twist, CH wag
	911	922	951	CCCH twist
	836	774	775	CC str., CCH bend
	506	520	525	CCC bend
A″	3 048	3 079	3 087	CH str.
	2 938	2 962	2 957 *	CH str.
	1 511	1 500	1 487	CC str., CCH bend
	1 396	1 397	1 389	CCH bend
	1 099	1 143	1 189	CC str., CCH bend
	1 037	980	927	HCCH, HCCC twist
	820	880	934	HCCC twist
	775	788	805	CCH wag

* From ref. 19.

TABLE 4

Distance ratios, r_{ij}, ordering parameters, $S_{\alpha\beta}$, and differences, ΔD_{ij} (Hz), between observed and calculated dipolar coupling constants for $[Re(CO)_4(C_3H_5)]$ dissolved in EBBA (see Table 1 for key)

(*a*) Completely planar allyl group

	Without vibrational averaging	With vibrational averaging
ΔD_{12}	0·89	0·82
ΔD_{13}	−4·08	−3·97
ΔD_{14}	−3·46	−2·95
ΔD_{15}	0·48	0·34
ΔD_{23}	0·83	0·83
ΔD_{24}	−1·58	−1·66

(*b*) Only protons 1,2,4, and 5 are coplanar

r_{14}/r_{12}	2·091 ± 0·005
r_{15}/r_{12}	1·853 ± 0·002
r_{24}/r_{12}	2·292 ± 0·005
$S_{xx} - S_{yy}$	0·0176 ± 0·002
S_{zz}	0·0236 ± 0·002

The η-allyl protons form an AA′BB′C spin system and hence must have either a C_2 axis passing along the C–H_3 bond, with non-planarity consisting of rotation of the two CH_2 groups into a staggered form, or a mirror plane relating protons 1,2,4, and 5 with H_3 displaced out of the plane. In each case the number of co-ordinates and $S_{\alpha\beta}$ values required to describe the structures is greater than

---

[17] N. J. D. Lucas, *Mol. Phys.*, 1971, **22**, 233.

[18] G. Davidson and D. C. Andrews, *J.C.S. Chem. Comm.*, 1972, 126.

[19] G. Davidson and D. C. Andrews, *J.C.S. Chem. Comm.*, 1972, 1381.

[20] G. Paliani, S. M. Murgia, G. Cardaci, and R. Cataliotti, *J. Organometallic Chem.*, 1973, **63**, 407.

[21] I. R. Beattie, N. Cheetham, M. Gardner, and D. E. Rogers, *J. Chem. Soc.* (*A*), 1971, 2240.

the number of observed proton dipolar couplings and hence the degree of non-planarity cannot be established. In order to get a complete description of the shape of the η-allyl group it would be necessary to measure the dipolar couplings between protons and ^{13}C nuclei. In the case where protons 1,2,4, and 5 are related by a mirror plane, and hence are coplanar, their relative positions can be determined and the result of such an analysis is given in Table 4. Vibrational averaging has been included and $r_{12} = 1{\cdot}871$ Å was taken as the standard internuclear distance.

We thank the S.R.C. for the award of a studentship (to R.M.S.) and Mr. M. C. McIvor, ICI Corporate Laboratories, Runcorn, for recording the 220 MHz spectrum.

[4/1609 *Received*, 1*st August*, 1974]