The splitting produced in praseodymium nitrite strongly suggests a similar bridging structure. For purposes of comparing band intensities, the spectrum of praseodymium nitrite is reproduced in Fig. 2.

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Invariance of Molecular 'Inverse' Force-constants

IN the quadratic form :

$$V = \tfrac{1}{2}\Sigma_1^n k_{rs}q_r q_s \qquad (k_{rs} = k_{sr}) \qquad (1)$$

representing the harmonic approximation to the potential energy of a vibrating molecule, the 'force constants' k_{rs} depend on the definition of the internal co-ordinates q_i used to represent small changes in the molecular configuration. For example, a full analysis[1] of the vibrations of $^{14}NO_2$ and $^{15}NO_2$, with co-ordinates q_1 and q_2 the NO bond stretches, gives for the stretch and stretch-interaction constants $k_{11} \equiv k_{22}$ and k_{12} the following values (in units 10^5 dynes/cm.) : (i) $10 \cdot 884$ and $1 \cdot 9914$ and (ii) $15 \cdot 507$ and $6 \cdot 614$ in the two cases where the third co-ordinate is (i) the ONO angle distortion and (ii) the change in OO distance. Thus the interpretation and comparison of force-constants obtained by different co-ordinate analyses present difficulties, which naturally increase with molecular complexity.

'Inverse' force-constants, h_{rs}, may be defined as the elements of the matrix $\{h_{rs}\}$ inverse to $\{k_{rs}\}$. A changed definition or choice of the internal co-ordinates q_r corresponds to a linear transformation, and the necessary invariance of V in (1) under this transformation implies that the h_{rs} can be transformed like the dyad or set of products $q_r q_s$. Thus if new co-ordinates $q_3, \ldots, q_n$ (linear combinations of the old $q_1, \ldots, q_n$) are chosen, leaving the old q_1 and q_2 as members of the new set, then the elements h_{11}, h_{12} and h_{22} are unchanged ; and in general, the inverse force-constants corresponding to any unchanged co-ordinates are invariant. This can be verified with precision by using full sets of force-constants k_{rs} for NO_2 in cases (i) and (ii) above.

This invariance of inverse force-constants holds similarly for the potential energy in the vibrations of a single symmetry class, where the k_{rs} are sym-

metry-co-ordinate force-constants, and a partial change is made in the choice of symmetry co-ordinates.

It has often been found useful tentatively to transfer one or more force-constants k_{rs} from one fully analysed molecule to another containing a similar atomic group. The present considerations suggest that it might be more suitable to transfer the corresponding inverse force-constants h_{rs}.

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Re-assessment of the Electron-spin Resonance Splitting Constants of Several Well-known Free Radicals

THE hyperfine splitting constants of the electron-spin resonance spectra of several well-known free radicals in solution have been re-measured recently. In some cases discrepancies with the values quoted in the literature have been found.

The particular case examined was the detection and identification by electron-spin resonance of a free radical produced during the thermal cracking of hydrocarbons, as the perinaphthenyl radical (it is hoped to publish details of this work in due course). It was found that the values of the splitting constants for the perinaphthenyl radical differed from those already reported[1]. In order to check the calibration of the magnetic field, the splitting constants of several well-known free radicals were measured, and the values obtained in the present work are compared with those reported in the literature in Table 1. The accuracy of the magnetic field calibration is confirmed by the agreement obtained for the last two free radicals listed. (Similar agreement has been obtained for several other free radicals.)

Table 1. HYPERFINE SPLITTING CONSTANTS FOR FREE RADICALS IN SOLUTION

Free radical	Hyperfine splitting (oersted)		Ref.
	This work	Literature	
Perinaphthenyl	$6 \cdot 30 \pm 0 \cdot 1$	$7 \cdot 3$	1
	$1 \cdot 82 \pm 0 \cdot 05$	$2 \cdot 2$	
DPPH *	$8 \cdot 9 \pm 0 \cdot 2$	10	2
B and K †	$11 \cdot 9 \pm 0 \cdot 2$	$13 \cdot 5 ; 11 \cdot 0$	2 ; 3
	$5 \cdot 9 \pm 0 \cdot 1$	$4 \cdot 9 ; 5 \cdot 7$	
Coppinger's ‡	$1 \cdot 45 \pm 0 \cdot 05$	$1 \cdot 0 ; 1 \cdot 3$	4 ; 5
p-Benzosemiquinone	$2 \cdot 34 \pm 0 \cdot 05$	$2 \cdot 368 \pm 0 \cdot 001$	6
		$2 \cdot 37 \pm 0 \cdot 01$	7
Hydrogen atom	512 ± 10	$505 \cdot 4 ; 508 \cdot 7$	8 ; 9

* α,α'-Diphenyl-β-picrylhydrazyl.
† 1,3 - Dimethyl - 1 - (phenylimineoxide) - butylidene - 3 - N' - phenyl - N' - oxynitrogen.
‡ 2,6 - Di-t-butyl-4-(3,5-di-t-butyl-4-oxocyclohexa - 2,5 - dienylidene methyl)phenoxy.

In view of the potential use of electron-spin resonance for identifying unknown free radicals, the need for an accurate measurement of the hyperfine splitting constants cannot be emphasized too strongly. The apparatus used for measuring the magnetic field was relatively simple, consisting of a proton resonance probe and a BC 221 crystal-controlled frequency meter. In most cases the derivative electron-spin