although the absolute magnitudes of these coupling constants are substantially lower than usual. This analysis of the n.m.r. spectrum, together with the fact that full hydrogenation yielded cyclotetradecane,[2] uniquely defines the structure and stereochemistry of the substance as II.

An X-ray crystallographic analysis of 1,8-bisdehydro[14]annulene (II) shows the crystals (from chloroform) to be monoclinic, $a = 8.685 \pm 0.012$ Å., $b = 7.789 \pm 0.008$ Å., $c = 8.086 \pm 0.010$ Å., $\beta = 113° 48'$; the space group is $P2_1/c$ (C^5_{2h}), which, with two molecules of $C_{14}H_{10}$ per unit cell, corresponds to a density of ρ calcd. = 1.182 g./cc. The unit cell dimensions and space group require that the molecule is centrosymmetric in the crystal. The crystal structure has been determined by trial and error, Fourier and least square methods, and fully confirms structure II (see Fig. 1). Accurate bond lengths and bond angles cannot, as yet, be reported, since rotational disordering of the molecules in the lattice, as indicated by diffuse scattering and large calculated Debye factors, has not been explicitly considered in the refinement analysis. A three-dimensional analysis of the crystal structure at 90°K. is being undertaken to obtain more accurate bond distances, and will be reported later (by N.A.B. and R.M.). At this stage, it is already apparent that all the carbon atoms are coplanar (± 0.03 Å.).

The striking difference in the chemical shifts of the inner and outer protons in the n.m.r. spectrum, together with the over-all geometry of the molecule as determined by the X-ray crystallographic analysis, clearly establishes 1,8-bisdehydro[14]-annulene to be aromatic. This is in keeping with expectation, since Hückel's rule is obeyed and the carbon skeleton is coplanar. The substance proved to be unusually stable; *e.g.*, it was completely unchanged after being kept for 1 month in the solid state at room temperature without protection from daylight. Also noteworthy is the position of the highest wave length maximum in the ultraviolet at 586 mμ (in isoöctane).[2]

Various aspects regarding the properties and synthesis of 1,8-bisdehydro[14]annulene are now under investigation. These include magnetic and theoretical studies of the electron distribution in the molecule, as well as the nature of the dehydrogenation involved in its formation.

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MEASUREMENT OF VERY FAST REACTION RATES BY RAMAN LINE BROADENING

Sir:

Line broadening measurements in magnetic resonance spectroscopy have been widely used to measure rates of fast chemical reactions.[1] It has been suggested[2] that line broadening techniques could also be used with various kinds of optical spectroscopy to measure the rates of even faster reactions. This has now been achieved, using Raman spectra. The range of usefulness seems to be for processes with half times from $\sim 10^{-11}$ to $\sim 10^{-14}$ sec. The latter probably is outside the range of chemical interest but the former is not, and for such rates the present method seems to be, by far, the most convenient when it is applicable. The present communication describes its application to the rate of proton transfer to trifluoroacetate ion from trifluoroacetic acid, probably *via* the hydronium ion, in aqueous solution.

Theory.—The Raman transition is assumed to involve degrees of freedom of the molecule which do not take part in the exchange. The effect of the exchange is to cause a time-dependence of the effective Hamiltonian "seen" by the portion of the molecule of interest: $H_{\text{eff}} = H_n$ when the molecule is in form n (n = 1, 2). A representation is used in which H_1 is diagonal, and off-diagonal elements of $(H_1 - H_2)$ are neglected.

The problem can now be treated by means of a simple generalization of the methods of Heitler.[3,4] In second-order time-dependent perturbation theory, the probability amplitude, b_f, for a transition in which the molecule changes its state and the angular frequency of a photon is decreased by ν obeys the equation

$$i\hbar\dot{b}_f = K_{fo}(t)\exp[i\int_0^t \omega_{fo}(t')dt'] - i\hbar\beta(t)b_f \quad (1)$$

Eq. (1) is to be compared with Heitler's eqs. (12) and (13).[3] The last term represents the broadening due to the natural line width. Otherwise, the only difference is in the time-dependence of K_{fo} and ω_{fo} due to the exchange. When the molecule is in form n, $K_{fo}(t) \equiv K_n$, $\omega_{fo}(t) \equiv \omega_n - \nu$, $\beta(t) \equiv \beta_n$. An explicit expression for K_{fo} is given by Heitler's eq. (7).[4]

The Raman intensity at frequency ν is given by eq. (2).

$$I(\nu)d\nu = 2Ad\nu \lim_{t\to\infty} \langle\beta(t)\ |b_f(t)|^2\rangle \quad (2)$$

Here $\langle\ \rangle$ indicates an average and A is a constant.

In the present case, the molecule jumps randomly back and forth between forms 1 and 2. If τ_n is the mean time of a single sojourn in form n, $1/\tau_1$ is k_1, the (pseudo) first-order rate constant for the reaction (form 1) → (form 2).

Equations (1) and (2) have been solved for the case of relatively slow exchange: $|\omega_1 - \omega_2|\,\tau_n >> 1$, and all $\beta_m\tau_n >> 1$. Since $|\omega_1 - \omega_2|$ may be as large as several hundred cm.$^{-1}$, this approximation should hold fairly well until τ_1 and τ_2 approach 10^{-14} sec. The result is eq. (3). Simplification

$$I(\nu) = \frac{2A}{\hbar^2}\left\{\left(\frac{\tau_1}{\tau_1+\tau_2}\right)|K_1|^2\frac{\beta_1 + 1/\tau_1}{(\nu-\omega_1)^2 + (\beta_1 + 1/\tau_1)^2} + \left(\frac{\tau_2}{\tau_1+\tau_2}\right)|K_2|^2\frac{\beta_2 + 1/\tau_2}{(\nu-\omega_2)^2 + (\beta_2 + 1/\tau_2)^2}\right\} \quad (3)$$

results if $|K_2|^2 << |K_1|^2$, or if $|\omega_1 - \omega_2| >> \beta_n + 1/\tau_n$. In these cases it is shown readily that eq. (4) gives

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[1] H. Strehlow, in "Investigation of Rates and Reaction Mechanisms, Part II," S. L. Friess, E. S. Lewis and A. Weissberger, Editors, Interscience Publishers, Inc., New York, N. Y., 1962, Chapter 7.

[2] M. Eigen, private conversations.

[3] W. Heitler, "The Quantum Theory of Radiation," 3rd edition, Clarendon Press, Oxford, 1954, pp. 136–145.

[4] *Ibid.*, pp. 189–196.

τ_1 in terms of β_1 and β, the half width at half height of the broadened line.

$$1/\tau_1 = \beta - \beta_1 \qquad (4)$$

Application.—Raman spectra of sodium trifluoroacetate ion in the presence of excess sodium hydroxide show an intense peak at 1433 cm.$^{-1}$ (probably the symmetrical C=O stretching frequency)[5] with a width at half height of 15.0 cm.$^{-1}$. In the presence of excess base the width is independent of trifluoroacetate concentration. Trifluoroacetate also has a fairly intense peak at 843 cm.$^{-1}$, with a width of 16.2 cm.$^{-1}$. Trifluoroacetic acid in the presence of excess HCl gives a strong peak at 816 cm.$^{-1}$ with a width of 28.8 cm.$^{-1}$. The latter two are presumably the C–C stretching frequencies.[5] In solutions containing trifluoroacetic acid, its conjugate base, and hydronium ion, the trifluoroacetate peak at 1433 cm.$^{-1}$ is broadened by as much as 7.2 cm.$^{-1}$, and the two peaks around 830 cm.$^{-1}$ both broaden and tend to merge. Both the 1433 cm.$^{-1}$ peak and the 816 cm.$^{-1}$ peak also tend to shift toward higher frequency by 2–5 cm.$^{-1}$ in mixed solutions. Spectra were measured on a Cary model 81 photoelectric Raman spectrophotometer, equipped with two Toronto-type mercury arc lamps. Solution temperatures were around 40°. The lines are roughly Lorentzian in shape.

The broadening of the 1433 cm.$^{-1}$ peak was used to obtain k_1 for trifluoroacetate ion by means of eq. (4). These results are shown in Table I. Solutions were made up simply by mixing trifluoroacetic acid and water. Concentrations were obtained by interpolation, using the degree of dissociation results of Redlich and co-workers.[6,7] Concentrations could also be inferred from the intensity of the 1433 cm.$^{-1}$ line in the Raman spectra. The average difference between the two estimates of the trifluoroacetate concentration was 10%. This strongly suggests that the intensity of the 1433 cm.$^{-1}$ band is proportional to the trifluoroacetate concentration and otherwise independent of the composition of the solution. Table I also gives the rate constant k_{-1} for the conversion of trifluoroacetic acid, as determined from the requirement that equilibrium be maintained.

TABLE I

AVERAGE LIFETIME OF TRIFLUOROACETATE ION IN VARIOUS SOLUTIONS

Molar			$10^{-11}\ k_1$	$10^{-11}\ k_{-1}$
$CF_3CO_2^-$	CF_3CO_2H	H^+	sec.$^{-1}$	sec.$^{-1}$
1.8	3.5	1.8	6.9	3.5
1.5	1.5	1.5	4.7	4.7
0.81	0.24	0.81	1.6	5.4

The rate constants cited above were used to calculate the shape of the doublet centering around 830 cm.$^{-1}$. The general shape of the band is moderately well reproduced. The band shape calculated by adding the unbroadened lines is worse, but the difference is not great. This evidence supports the interpretation that the broadening is due to exchange.

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[5] R. E. Robinson and R. C. Taylor, *Spectrochimica Acta*, **18**, 1093 (1962).

[6] O. Redlich and G. C. Hood, *Discussions Faraday Soc.*, No. 24, 87 (1957).

[7] G. C. Hood, O. Redlich and C. A. Reilly, *J. Chem. Phys.*, **23**, 2229 (1955).

[8] Alfred P. Sloan Foundation Fellow, 1960-1964.

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GLYCEROL AS A PRECURSOR OF RICININE[1]

Sir:

By means of tracer experiments with young *Ricinus communis* L. we have recently established[2,3] that succinic acid, or a closely related four-carbon dicarboxylic acid found in the Krebs tricarboxylic acid cycle, is a specific precursor of carbon atoms 2, 3, and 7 in the biosynthesis of ricinine I.

Since an origin outside of the Krebs cycle was indicated for carbon atoms 4, 5, and 6, glycerol-1-^{14}C and glycerol-2-^{14}C were fed in separate experiments to young *Ricinus* plants. The percentages of the incorporated radioactivity located at the O-methyl, N-methyl, and nitrile carbon atoms of the isolated ricinine have been reported already.[2]

We now wish to describe degradative procedures to isolate the carbon atoms at positions 4, 5, and 6 of the ricinine molecule, and applications of these procedures to the ricinine obtained from both glycerol-1-^{14}C and glycerol-2-^{14}C, as well as, in part, to ricinine from the previously reported succinic acid-2,3-^{14}C and sodium acetate-2-^{14}C feeding experiments.[2,3]

Ricinine I was converted to 4-methoxy-1-methyl-2-pyridone II, m.p. 114–116°,[4] which was reduced with lithium aluminum hydride to 1-methyl-4-piperidone III, b.p. 55–60° (12 mm.),[5] identified by comparison with an authentic sample. Reaction of III with phenyllithium provided the known 4-hydroxy-1-methyl-4-phenylpiperidine[6] IV, m.p. 115–116°, which was oxidized with potassium permanganate to benzoic acid V, m.p. 121–122°, with the carboxyl carbon atom originating from carbon 4 of ricinine.

Nitration of ricinine I afforded the 5-nitro derivative VI, m.p. 163–164° (*anal.* Calcd. for $C_8H_7O_4N_3$: C, 45.94; H, 3.37; N, 20.09. Found: C, 45.94; H, 3.39; N, 20.19) which on treatment with calcium hypobromite yielded tribromonitromethane (bromopicrin) VII, with the carbon atom originating from position 5 of ricinine. The bromopicrin was identified by comparison with an authentic sample prepared from picric acid.[7]

Catalytic reduction of the pyridone II yielded 1-methyl-2-piperidone VIII, b.p. 110–105° (12 mm.) (mercuric chloride derivative, m.p. 117–120°[8]) which was hydrolyzed with hydrochloric acid,

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[1] N.R.C. No. 7107.

[2] P. F. Juby and Léo Marion, *Biochem. Biophys. Res. Comm.*, **5**, 461 (1961).

[3] P. F. Juby and Léo Marion, *Can. J. Chem.*, in the press.

[4] E. Winterstein, J. Keller and A. B. Weinhagen, *Arch. Pharm.*, **255**, 513 (1917).

[5] R. E. Lyle, R. E. Adel and G. G. Lyle, *J. Org. Chem.*, **24**, 342 (1959).

[6] Aktieselskabet "Ferrosan," Danish Patent 60,592 (1943); *Chem. Abs.*, **40**, 4086^5 (1946).

[7] J. Baddiley, G. Ehrensvärd, E. Klein, L. Reio and E. Saluste, *J. Biol. Chem.*, **183**, 777 (1950).

[8] C. Räth, *Ann.*, **489**, 107 (1931).