To obtain reproducible light scattering values, it was necessary to avoid exposing the solutions to temperatures above 20° and to centrifuge at concentrations *below 0.2%* at 40,000 *g* for several hours. Centrifugation at higher concentrations yielded light scattering values as much as double that reported above but the other measurements remained essentially unchanged. This behavior is consistent with the existence of a very small fraction of the solute in the form of side-by-side aggregates. This may account in part for the much higher values obtained by others using this method.

Evidence for the shape of the particle can be obtained from the shape of the reciprocal scattering envelope now that polydispersity has been shown to be low. These data are matched within 5% by the envelope of a rod-shaped particle of 3000 Å. length. The intrinsic viscosity yields an axial ratio of 170. In this range the sedimentation constant is almost entirely dependent on diameter and corresponds to 17 Å. for an ellipsoid, 14 Å. for a cylinder. This leads to an ellipsoid length of 2900 Å. In addition to the above mentioned flow birefringence data, based on extinction angle measurements, the variation of the specific birefringence with gradient was characteristic of that of a rod. Finally, the absence of a polyelectrolyte effect in the reduced specific viscosity upon lowering the ionic strength insured the rigidity of the rod-like particle.

Inasmuch as this particle appears to embody the essential characteristics of a building unit postulated by Schmitt, Gross and Highberger[2,3] from which the three different structural forms of collagen are formed, it may be proper to give it the name tropocollagen suggested by these authors.

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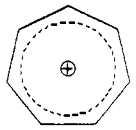
THE VIBRATIONAL SPECTRUM AND STRUCTURE OF THE TROPYLIUM ION

Sir:

Doering and Knox[1] have recently prepared cycloheptatrienylium (tropylium) bromide and obtained chemical and physical properties which indicate that the tropylium ion represents a new aromatic system the relative stability of which is due to resonance resulting from the presence of six (π) electrons in the conjugated unsaturated seven membered ring. As part of a program of studying the Raman spectrum of colored substances we have obtained the Raman spectrum of tropylium bromide and we wish to give here a preliminary report of the vibrational spectrum of the tropylium ion. This spectrum supports the conclusion of Doering and Knox that this ion represents a new aromatic system.

The Raman spectra were obtained on a Hilger E 612 Spectrograph having a camera aperture of F 5.4 and using Hg 5461 Å. excitation. Because of the photochemical reactivity of the tropylium ion, extremely heavy optical filtering was required to eliminate all blue radiation from the sample. The filters used were saturated K_2CrO_4 and $NdCl_3$ solutions and a Kodak Wratten #55 filter. The spectra were obtained in 25% hydrobromic acid solution, and a typical concentration of tropylium bromide in this solution was about 1 mole/liter. As with ferrocene it was found that an optimum concentration exists for obtaining the maximum intensity of scattered radiation at a given wave length.[2] There was no photochemical decomposition of the sample under prolonged exposure to Hg 5461 Å. radiation. Infrared spectra were obtained in HBr solution and KBr pellet using a Perkin-Elmer model 12c Spectrometer. The infrared spectrum in a KBr pellet has been reported by Doering and Knox.[1] The Raman and infrared spectra in HBr solution are collected in Table I. The observed Raman and infrared frequencies of benzene corresponding to the allowed fundamental modes of vibration are also given for comparison.

A study of the vibrational spectrum of the tropylium ion reveals the following features: (1) The Raman and infrared spectrum are remarkably simple for a system having thirty-six vibrational degrees of freedom, indicating a structure of high symmetry. (2) There are no coincidences between Raman and infrared frequencies, indicating a structure of high symmetry. (3) The position, distribution and relative intensities of the observed frequencies are readily interpreted in terms of an aromatic system, and there is good correlation with the corresponding frequencies of benzene. These features are all consistent with a planar aromatic structure having D_{7h} symmetry.



The selection rules for such a structure predict no coincidences with seven Raman ($2A_1'$, $1E_1''$, and $4E_2'$) and four infrared ($1A_2''$, and $3E_1'$) active fundamentals. These numbers agree remarkably well with the observed spectrum of seven Raman lines and four relatively strong infrared peaks. The two totally symmetric A_1' fundamentals are readily assigned to the 868 cm.$^{-1}$ and 3065 cm.$^{-1}$ Raman lines as the ring breathing and C–H stretching modes, respectively. Their intensity and appearance indicate that they are probably polarized as expected from the selection rules. A comparison of the spectrum of tropylium ion with that of benzene shows a number of expected similarities. In the Raman spectrum the C–H stretching frequencies appear at 3065 cm.$^{-1}$, the C–H in plane bending frequencies appear near 1200 cm.$^{-1}$, and the C–H out of plane bending near 900 cm.$^{-1}$, all quite close to the corresponding frequencies in benzene. Of the Raman active skeletal frequencies one

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[1] W. von E. Doering and L. H. Knox, THIS JOURNAL, **76**, 3203 (1954).

[2] E. R. Lippincott and R. D. Nelson, *J. Chem. Phys.*, **21**, 1307 (1953).

would expect the multiple bond frequency to remain near where it is observed in benzene. The ring breathing and the in-plane ring distortion frequencies should appear lower because of their dependence upon the size of the ring. In agreement with this the multiple bond frequency of the tropylium ion occurs at 1594 cm.$^{-1}$ as compared to 1596 cm.$^{-1}$ for benzene. The ring breathing mode dropped from a value of 992 cm.$^{-1}$ in benzene to a value of 868 cm.$^{-1}$ in the tropylium ion. The 606 cm.$^{-1}$ in-plane bending frequency of benzene drops to 433 cm.$^{-1}$ in the tropylium ion. Similar considerations apply to a comparison of their infrared spectra. It is significant that there are no Raman frequencies observed from 1600–1700 cm.$^{-1}$ A conjugated non-aromatic system of double bonds gives one or more very strong Raman lines in this region. The failure to observe such lines can be taken as further evidence for the aromatic nature of the tropylium ion.

TABLE I

THE VIBRATIONAL SPECTRUM OF TROPYLIUM ION COMPARED WITH THAT OF BENZENE

Key: vs = very strong; s = strong; m = medium; mw = medium weak; w = weak.

Raman				Infrared			
$C_7H_7^+$ cm.$^{-1}$	I	C_6H_6[a] cm.$^{-1}$	I	$C_7H_7^+$ cm.$^{-1}$	I	C_6H_6[a] cm.$^{-1}$	I
433	m	605	m	633	s	671	s
		849	mw	658	m		
868	vs	992	vw	992	mw	1037	s
925[b]	w						
1210	mw	1178	m	1222	w		
				1278	w		
1594	m	1585	m	1477	vs	1485	s
		1606					
				2060	w	1807	m
						1964	m
		3047	s	3020	s	3405	s
3045–3085[c]	s	3062	vs	3080	w	3099	s

[a] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules" D. Van Nostrand Company, Inc., New York, 1945, p. 364–365. [b] This line was obtained on only two plates. [c] The intensity distribution of this broad band is asymmetrical and represents two incompletely resolved lines.

The authors are greatly indebted to Professor Doering and Dr. Knox for supplying us with a sample of tropylium bromide to carry out the work.

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CYTIDINE DIPHOSPHATE CHOLINE: A NEW INTERMEDIATE IN LECITHIN BIOSYNTHESIS[1]

Sir:

Two pathways for the biosynthesis of lecithin occur in mammalian liver preparations. Pathway I incorporates free choline into the lecithin molecule by a reaction sequence which does not involve the intermediary formation of phosphorylcholine[2] but does require ATP[3] and CoA.[4] A thiophosphate ester of CoA, phosphatidyl CoA, has been suggested as an intermediate.[4]

In pathway II, discovered by Kornberg and Pricer,[5] phosphorylcholine is incorporated as a unit into the lecithin structure. We have now found that the washed rat liver mitochondrial preparations already shown to catalyze the reactions of pathway I also catalyze the reactions of pathway II, but the conditions required are very different (Table I).

TABLE I

PROPERTIES OF ENZYME SYSTEMS FOR LECITHIN BIOSYNTHESIS

	Pathway I	Pathway II
Active precursor	Choline	Phosphorylcholine
*p*H optimum	9.4	7.0
Fluoride inhibition	0	+
Needed cofactors: ATP	+	0
CoA	+	0
CTP	0	+

Relatively large amounts of ATP (Pabst lot 116, *ca.* 95% pure) were at first found to support the reactions of pathway II, but when crystallized ATP (Pabst lot 122) was substituted no activity was observed. Further investigation led to the discovery of a highly specific requirement for CTP as seen in Table II. The activity of the less pure ATP lot 116 is explained by its content (<1%) of CTP. The addition of inorganic pyrophosphate markedly reverses the stimulation observed with added CTP.

TABLE II

COFACTOR REQUIREMENT FOR PATHWAY II

	Added cofactors	Lecithin synthesized (total counts)
1	5 μM of ATP lot 116	590
2	5 μM of ATP lot 122	20
3	5 μM of ATP lot 122 + 0.5 μM ITP	0
4	5 μM of ATP lot 122 + 0.5 μM UTP	50
5	5 μM of ATP lot 122 + 0.5 μM GDP	57
6	5 μM of ATP lot 122 + 0.5 μM CTP	1677
7	5 μM of ATP lot 122 + 0.5 μM CTP + 2.5 μM inorganic pyrophosphate	750

Each tube contained 10 μM $MgCl_2$, 50 μM of phosphate buffer, *p*H 7.4, 3 μM of phosphorylcholine-P^{32} (113,000 cts./μM) and 25 mg. of lyophilized mitochondria in a total volume of 1.0 ml. Incubated at 37° for 1 hour. Phospholipide counted as previously described.[2]

The following abbreviated reaction scheme was postulated to explain the activation of this system by CTP and its reversal by inorganic pyrophosphate:

$$\text{(1)}\quad \text{CTP} + \text{phosphorylcholine} \rightleftarrows \text{cytidine diphosphate choline} + \text{pyrophosphate}$$

$$\text{(2)}\quad \text{Cytidine diphosphate choline} + \text{acceptor} \longrightarrow \text{lecithin} + \text{CMP}$$

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(2) E. P. Kennedy, *J. Biol. Chem.*, **209**, 525 (1954).

(3) Abbreviations: ATP, adenosine-5'-triphosphate; CoA, coenzyme A; CTP, cytidine-5'-triphosphate; UTP, uridine-5'-triphosphate; ITP, inosine-5'-triphosphate; GDP, guanosine-5'-pyrophosphate.

(4) E. P. Kennedy, *Federation Proc.*, **13**, 241 (1954).

(5) A. Kornberg and W. E. Pricer, Jr., *ibid.*, **13**, 241 (1952).