electron from the leuco dye. It would not react further to give the blue form since basic glucose is a strong reducing agent. Any diradical (red species) formed could be converted easily to leuco dye in such strongly reducing environment.

Alternatively, the red species could be an entrapped excited triplet state of the leuco form. The absorption and fluorescence then would arise from triplet–triplet transitions. Extremely high viscosities would favor the stability of the triplet by inhibition of configurational changes necessary for conversion to the singlet ground state of the leuco dye. The stability of the triplet state would be even further enhanced by interaction with the medium as is indicated by the small shifts in absorption spectra of the red species in the dif-

ferent glasses. Recently we found that leuco dye glasses give only the blue form when exposed to ionizing radiation.[17] It is known that triplet states of aromatic compounds produced by ultraviolet light cannot, however, be produced by ionizing radiation in analogy with our system.

One might also postulate that the colored forms arise from expulsion of electrons yielding a different type of semiquinone and an electron trapped in the medium. We have not, however, found the near infrared absorption considered to be characteristic of entrapped electrons.[18]

(17) G. Oster and B. Broyde, details to be published.
(18) H. Linschitz, M. G. Berry and D. Schweitzer, THIS JOURNAL, **76**, 5833 (1954).

BROOKLYN, N.Y.

The Cyclic Structures of Methylene Aniline and Methylene-*p*-toluidine. A Dipole Moment Study

BY ROBERT A. FLORENTINE AND JOHN G. MILLER

The electric moments of trimeric methylene-aniline and trimeric methylene-*p*-toluidine have been measured in benzene, carbon tetrachloride and ligroin. The former has an average moment of 1.17 D, and the latter, 0.89 D. These moments support the assignment of a *sym*-triazane ring configuration to these trimers and indicate that the rings are of the chair form. The pyramidal arrangement of the valence bonds of the nitrogen atoms appears to be flattened greatly in these rings.

Reaction of aniline with formaldehyde in water or alcohol at 0° produces nearly exclusively trimeric methylene aniline, $(C_6H_5NCH_2)_3$. Similarly, *p*-toluidine gives trimeric methylene-*p*-toluidine, $(CH_3C_6H_4NCH_2)_3$. These polymeric compounds appear to possess fixed cyclic structures containing the *sym*-triazane ring
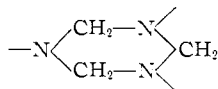
as revealed by the definiteness of their molecular weights and melting points and by their reduction-cleavage into amine, methylated amine and dimethylated amine.[1]

This paper presents further evidence for the cyclic structures of these trimers. This evidence comes from measurement of their dipole moments and shows that the molecules are probably in strainless chair forms, with the pyramids of valence bonds of the nitrogen atoms flattened nearly to a coplanar arrangement.

Experimental

Solvents.—C.P. benzene was refluxed over sodium for 30 minutes and then distilled through a 16-inch packed column (glass helices) under high reflux. The product was stored over sodium until used; b.p. 80.2° cor., $n^{30}D$ 1.4983, d^{30} 0.8737. C.P. carbon tetrachloride was distilled through the same column; the fraction boiling at 76.2° was collected and stored over MgSO₄; d^{30} 1.5850, $n^{30}D$ 1.4574. "High boiling" ligroin, a mixture of hydrocarbons boiling from 68 to 105°, was stored over sodium, a single stock being used throughout any dipole moment determination. Transfer of solvent and solutions to the measuring equipment was carried out under

dry air pressure in all-glass apparatus to prevent evaporation and contamination.

Other Materials.—Baker C.P. aniline was freshly refluxed over zinc dust and distilled under reduced pressure. The formaldehyde was Baker C.P. grade (36% solution in water). Matheson C.P. *p*-toluidine was crystallized from cold anhydrous ethanol. The samples used melted at 44.5° cor.

Preparation of the Trimers.—The preparation of the crystalline trimers of methylene aniline and methylene-*p*-toluidine followed essentially the method of Miller and Wagner.[1] The purification of the methylene aniline was accomplished by a series of extractions and crystallizations with absolute ethanol. The recrystallized trimer was kept in a vacuum desiccator, m.p. 141.0° cor. The methylene-*p*-toluidine was recrystallized from ligroin, m.p. 128.1° cor.

Measurements.—The dielectric constants were determined by use of a radiofrequency bridge over a range of frequencies from 0.5 to 1.5 megacycles, the measurements and calculations being made according to the procedures outlined previously.[2] The values of refractive index were determined[3] with a Pulfrich refractometer, using the Na_D, H_α and H_β lines. The Drude function $1/\phi = (n^2 + 2)/(n^2 - 1)$ was calculated for each of the frequencies and then extrapolated linearly to zero frequency, whereby n^2 was obtained for infinite wave length for each solution. Densities were measured with a pycnometer of approximately 25-cc. volume. A large oil-bath kept at 30 ± 0.005° was used to control the temperature for all the measurements. Each trimer was measured at five different concentrations in each solvent. In benzene and CCl₄ these concentrations lay in the mole fraction range from 0.001 to 0.01. In ligroin, methylene aniline was studied at weight fractions from 0.0003 to 0.0012 and methylene-*p*-toluidine from 0.0002 to 0.0025.

Calculation of the Dipole Moment Values.—The dielectric constant ϵ_{12}, density d_{12}, and square of the refractive index for infinite wave length $n_{12}{}^2$, for the solutions were treated as linear functions of the mole fraction of the solute N_2, for the benzene and CCl₄ solutions and as linear functions of the weight fraction of the solute w_2, for the ligroin solutions. The least squares values are shown in Table I. The slope

(1) J. G. Miller and E. C. Wagner, THIS JOURNAL, **54**, 3698 (1932).

(2) J. G. Miller, *ibid.*, **60**, 42 (1938); **64**, 117 (1942).
(3) J. G. Miller, *ibid.*, **56**, 2360 (1934).

TABLE I

THE DENSITY, DIELECTRIC CONSTANT AND SQUARE OF THE REFRACTIVE INDEX FOR INFINITE WAVE LENGTH AS LINEAR FUNCTIONS OF THE CONCENTRATION FOR SOLUTIONS OF THE TRIMERS IN DIFFERENT SOLVENTS AT 30°

Solvent	Property	Methylene aniline	Methylene-p-toluidine
Benzene	d_{12}	$0.86713(\pm0.00002) + 1.1278(\pm0.0016)N_2$	$0.86726(\pm0.00012) + 0.8013(0.0068)N_2$
	ϵ_{12}	$2.26232(\pm0.00010) + 3.5041(\pm0.0067)N_2$	$2.26225(\pm0.00006) + 2.1267(\pm0.0019)N_2$
	$n_{12}{}^2$	$2.16190(\pm0.00012) + 1.8198(\pm0.0094)N_2$	$2.16178(0.00006) + 1.3488(\pm0.0098)N_2$
CCl₄	d_{12}	$1.58808(\pm0.00012) + 2.0157(\pm0.0025)N_2$	$1.58825(\pm0.00002) + 2.2541(\pm0.0030)N_2$
	ϵ_{12}	$2.21790(\pm0.00008) + 6.4131(\pm0.0088)N_2$	$2.21769(\pm0.00008) + 6.1378(\pm0.0018)N_2$
	$n_{12}{}^2$	$2.11679(\pm0.00010) + 4.5272(\pm0.0080)N_2$	$2.11174(\pm0.00008) + 1.5278(\pm0.0080)N_2$
Ligroin	d_{12}	$0.69197(\pm0.00040) + 0.1172(\pm0.0040)w_2$	$0.69212(\pm0.00002) + 0.86447(\pm0.00027)w_2$
	ϵ_{12}	$1.92978(\pm0.00102) + 0.4138(\pm0.0060)w_2$	$1.92342(\pm0.00012) + 0.2210(\pm0.0014)w_2$
	$n_{12}{}^2$	$1.8390(\pm0.0040) + 0.1752(\pm0.0020)w_2$	$1.83874(\pm0.00008) + 0.1716(\pm0.0090)w_2$

and intercept terms then were used to calculate the dielectric polarization P_{20} and molar refraction R, of the solute at infinite dilution and infinite wave length, using the Hedestrand[4] equation for the benzene and CCl₄ solutions and the procedures of Li and Chu[5] for the ligroin solutions. Table II gives the values of P_{20} and R so obtained and the values of the dipole moments μ, derived from them by the equation, $\mu = 0.01281 [(P_{20} - R)T]^{1/2}$.

TABLE II

THE POLARIZATION, MOLAR REFRACTION AND DIPOLE MOMENTS OF THE TRIMERS IN THE DIFFERENT SOLVENTS AT 30°

Trimer	Solvent	P_{20}	R	μ (debyes)
Methyleneaniline	Benzene	125.07	97.00	1.18
	CCl₄	126.56	98.79	1.17
	Ligroin	126.12	98.92	1.16
Methylene-p-toluidine	Benzene	128.96	112.80	0.896
	CCl₄	128.78	112.70	.893
	Ligroin	127.83	112.43	.873

The theoretical values of the molar refraction based on sym-triazane ring structures are nearly the same as the values given for R in Table II. Calculations based on atomic refractions[6] give D-line molar refractions of 98.00 for the methylene aniline and 111.85 for the methylene-p-toluidine and Hα-line values of 97.21 and 111.00, respectively. The values calculated from D-line bond refractions[7] are 97.89 and 111.72.

Infrared Absorption Spectra.—The infrared absorption spectra were measured for CCl₄ solutions of the trimers by Mr. Ralph A. Brown at the laboratory of the Atlantic Refining Company. A Beckman IR-2 instrument was used. The presence of three phenyl groups per molecule made it unfeasible to carry out an analysis of the spectra such as used for the analogous substance, trioxane, by Ramsay.[8] Nevertheless, the spectra revealed that the two trimers have closely similar structures, the locations and intensities of the many prominent bands being the same for the two.

Discussion

The molecules under discussion, trimeric methylene aniline and trimeric methylene-p-toluidine are nitrogen-system counterparts of trimethylene oxide (trioxane) and trimethylene sulfide (trithiane). The dipole moments[9,10] of the latter two substances have been shown to be in accord with chair forms, in agreement with the results of the X-ray,[11]

(4) G. Hedestrand, Z. physik. Chem., **B2**, 428 (1929).

(5) N. C. C. Li and T.-L. Chu, THIS JOURNAL, **69**, 558 (1947).

(6) K. Fajans in "Physical Methods of Organic Chemistry," Vol. I, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1945, p. 673.

(7) H. R. Davidson, J. Chem. Ed., **27**, 598 (1950).

(8) D. A. Ramsay, Trans. Faraday Soc., **44**, 289 (1948).

(9) A. A. Maryott and S. F. Acree, J. Research Natl. Bur. Standards, **33**, 71 (1944).

(10) K. E. Calderbank and R. J. W. LeFèvre, J. Chem. Soc., 199 (1949).

(11) N. F. Moerman, Rec. trav. chim., **56**, 161 (1937).

electron diffraction,[12] infrared[8] and Raman[13] spectroscopic studies of those cyclic compounds. Our compounds present a more complicated problem because of the phenyl groups attached to the nitrogen atoms. If the valence bonds of the nitrogen atoms are in fixed pyramidal arrangement and the carbon bonds are distributed in fixed tetrahedral manner, then ten different strainless conformations can be pictured for either trimer, four of the chair form and six of the boat form.

Figure 1 shows one of the chair forms, with Ph representing the phenyl group or p-tolyl group. The nitrogen and carbon valency angles are symbolized α and β, respectively, θ is the dihedral angle between the plane of the C–N–C bonds in the ring and the plane of the three methylene carbon atoms, while δ is the angle between the N-Ph axis and the bisector r, of the CH₂–N–CH₂ angle. These angles, θ and δ will be determined by α and β as follows, $\cos \theta = [2 \sin (\beta/2) - \sin (\alpha/2)]/[\sqrt{3} \cos (\alpha/2)]$ and $\cos \delta = (\cos \alpha)/[\cos (\alpha/2)]$.

The bond and group moments will be symbolized as: H→C $= m$, C→N $= h$, and Ph→N $= g$. For all of the isomeric forms, the moments of the bonds attached to the methylene carbon atoms may be resolved completely into three moments, one along each of the C–N–C bisectors r, and pointing toward the N atom. Each of these moments will have the magnitude $r = 2(h + m)\cos(\alpha/2)$.

The moment of each isomer can be given in terms of g, r, δ and θ. Table III lists the moments of the chair forms in these terms. In order to distinguish these forms, it will be convenient to adopt the terminology generally applied to the extracyclic bonds and substituents of the cyclohexane ring. In this way, the form shown in Fig. 1 may be called the eee form, and it is easily seen that the three other forms would be symbolized as in Table III, depending upon whether the Ph groups are attached equatorially (e) or axially (a).

The most certain information that can be obtained from the data in Table II concerns the effect of the introduction of a methyl group in the para position in Ph. This effect, a decrease of about 0.28 D in the moment, is most helpful in relating the moments to the structures of the trimers. Such a methyl group should contribute a moment equal to a single H→C moment and this moment

(12) O. Hassel and H. Viervoll, Acta Chem. Scand., **1**, 149 (1947).

(13) L. Kahovec and K. W. F. Kohlrausch, Z. physik. Chem., **B35**, 29 (1937).

TABLE III

THE FORMULAS FOR THE MOMENTS OF THE FOUR CHAIR
FORMS OF THE TRIMERS

Form	Moment
eee	$3g \sin(\theta + \delta) + 3r \sin \theta$
aee	$[(3g \sin \theta \cos \delta + g \cos \theta \sin \delta + 3r \sin \theta)^2 + (2g \sin \theta \sin \delta)^2]^{1/2}$
aae	$[(3g \sin \theta \cos \delta - g \cos \theta \sin \delta + 3r \sin \theta)^2 + (2g \sin \theta \sin \delta)^2]^{1/2}$
aaa	$3r \sin \theta - 3g \sin(\delta - \theta)$

should lie along the axis attaching the phenyl group to the nitrogen atom. Marsden and Sutton[14] have shown that such a methyl group in N-dimethyl-*p*-toluidine is not likely to interact with the dimethylamino group. It would, therefore, appear rather certain that if the *g* vector is equal to *h* in the methylene aniline trimer, then it is simply *h* + *m* in the other trimer. Now, since *r* most probably is the same for both of the trimers, much weight is taken off the uncertainty in the value to be assigned to *h*. In this situation, the parameter most greatly affecting the moment will be *α*, the valency angle of nitrogen, for it is the variation in *α* which most greatly affects the summation of the *g* and *r* values.

Table IV contains values of the dipole moments for the chair forms calculated for different values of *α*, with *β* fixed at the regular tetrahedral value, 109.5°. In these calculations, the formulas of Table III were used with these values of the bond and group moments: *m* = 0.40, *h* = 0.45, *g* = 0.45 (for methylene-aniline) or 0.85 (for methylene-*p*-toluidine).

TABLE IV

THE DIPOLE MOMENTS OF THE CHAIR FORMS OF THE
TRIMERS[a] AS A FUNCTION OF THE NITROGEN VALENCY
ANGLE, α

α		109.3°	115°	118°	120°
eee	A	2.16	1.60	1.17	0.56
	T	2.57	1.73	1.06	0
aee	A	1.62	1.16	0.87	0.56
	T	1.64	1.00	.57	0
aae	A	1.05	0.71	.56	0.56
	T	0.86	.56	.38	0
aaa	A	.36	.18	.21	0.56
	T	.84	.95	.76	0

[a] A = trimeric methylene-aniline; T = trimeric methylene-*p*-toluidine.

The moments given in Table IV indicate strongly that the trimers exist in either the eee or aee form and have high values of *α* (115 to 119°). These two forms are very similar at the high *α* values and are both sterically unstrained at all reasonable assignments of *α* and *β*. The aae form would not possess the observed dipole moments at these high *α*-values and is sterically impossible at the lower *α*-values needed to produce satisfactory agreement of the moments. The aaa form does not show any indication of having the observed moment at any choice of *α*; the calculated moments pass through a maximum for the one substance and through a minimum for the other at about 115°. This conformation is also sterically impossible at lower *α* due to the bulk of the *φ*-groups.

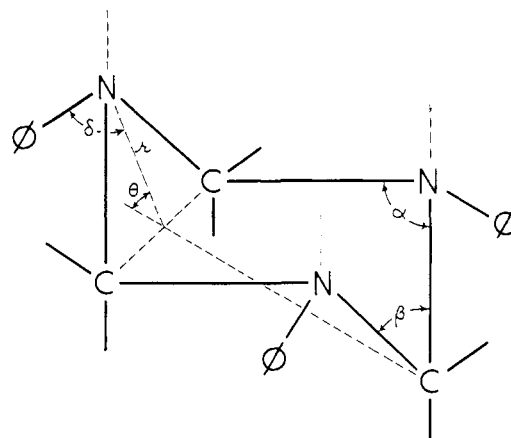(14) R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, 599 (1936).

Fig. 1.—The *sym*-triazane ring of the trimers in the chair conformation. In this example the *φ*-groups are all attached equatorially (*φ* is phenyl).

As expected from the fact that *β* enters the equations only as one of the factors determining *θ*, the value of the carbon valency angle seems to have relatively little effect on the moments. Thus, if *β* is taken as 107.5° or 111.5° instead of 109.5°, the moments in Table IV change by only 0.05 *D* at each *α* for the eee and aee forms of methylene aniline and even less for the other trimer. To check the small effect of the moment assigned to the C→N bond, a value of 0.23 *D* was used and the moments for the eee and aee forms were recalculated. The results showed little change in the values of *α* required to give the observed moments.

The boat forms have been considered and found improbable. Six of these can be pictured with *α* and *β* at the same fixed values in each ring but with the Ph groups oriented differently. Using the "flagpole" (fp) and "bowsprit" (bs) symbols to distinguish the possible orientations of Ph attached to the one nitrogen atom and the *be* and *ba* symbols for the orientations of Ph attached to either of the other two nitrogen atoms, these six boats can be represented as follows: (bs, be, be), (bs, be, ba), (bs, ba, ba), (fp, be, be), (fp, ba, be), (fp, ba, ba). Four of these are readily interconvertible by twisting the rings, *i.e.*, by simultaneous changes in *α* and *β* involving only slight strains during the course of interconversion. The other two, (fp, be, be) and (bs, ba, ba), are similarly readily interconvertible with each other but not with the other four.

The moments of the six boat forms have been formulated and the values calculated for different values of *α*. In no case does the boat fit the observed moments of the trimers, the calculated moments being generally too low. As *α* approaches 120°, the boat forms become identical and have a moment one-third that of the chair form. As *α* decreases, the moments remain too low for most of the boat forms or else give values for the trimeric methylene-*p*-toluidine which are monotonously higher than those of the other trimer. All but two of these boats are so highly encumbered as to be impossible without great strain and in view of their interconvertibilities all of the boats would appear to be less stable conformations than the

melting points and other physical properties of the compounds would lead one to expect.

In conclusion, it appears that these trimers are both in the chair form with nearly coplanar arrangements of the valence bonds of the nitrogen atoms. The latter feature is not surprising, to judge from the dipole moments and other properties of aromatic amines which yield values of the nitrogen valency angle. The attachment of a phenyl group to nitrogen seems to widen the valency angle of that atom. Such attachment apparently causes a change in the nitrogen bonding orbitals from sp^3 to sp^2 hybridization, with the lone pair of nitrogen

electrons now in symmetric p-orbitals at right angles to the plane of the bonding orbitals. In this situation, the contribution of the lone pair to the molecular moment diminishes and the calculations made above are the more valid.

[Contribution from the John Harrison Laboratory of Chemistry, University of Pennsylvania]

# The Preparation of Di-n-butylboron Cyanide by the Interaction of Di-n-butylboron Chloride with Trimethylsilyl Cyanide[1]

By E. Charles Evers, Walter O. Freitag, William A. Kriner and Alan G. MacDiarmid

The interaction of $(n\text{-}C_4H_9)_2BCl$ with $(CH_3)_3SiCN$ results in the formation of the new polymeric compound $(n\text{-}C_4H_9)_2BCN$ which is a viscous liquid of high molecular weight. $(n\text{-}C_4H_9)_2BCN$ may also be prepared by the reaction of $(n\text{-}C_4H_9)_2BCl$ with AgCN. This substance when treated with sodium in liquid ammonia produces monomeric $(n\text{-}C_4H_9)_2BNH_2$, previously known only in a more highly polymerized form. $(CH_3)_3B$ and $(CH_3)_3SiCN$ react to produce a complex mixture of substances.

Introduction

In a preceding paper[2] it was shown that B_2H_6 reacts with trimethylsilyl cyanide to form an addition compound which, on heating, decomposes to form a polymeric substance, BH_2CN. Reaction proceeds according to the equation

$$(CH_3)_3SiCN\cdot BH_3 \longrightarrow (CH_3)_3SiH + BH_2CN \quad (1)$$
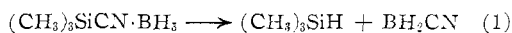
The present investigation was undertaken in an attempt to prepare less highly polymerized materials by replacing H with alkyl groups. For this purpose we have studied the reaction of trimethylsilyl cyanide with $(n\text{-}C_4H_9)_2BCl$ and $(CH_3)_3B$.

Results and Discussion

Di-n-butylboron chloride reacts rapidly and quantitatively with trimethylsilyl cyanide without the formation of any apparent addition compound under our experimental conditions. Reaction proceeds according to the equation
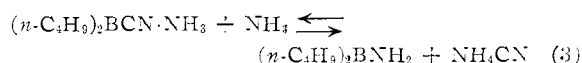
$$(n\text{-}C_4H_9)_2BCl + (CH_3)_3SiCN \longrightarrow$$
$$(n\text{-}C_4H_9)_2BCN + (CH_3)_3SiCl \quad (2)$$
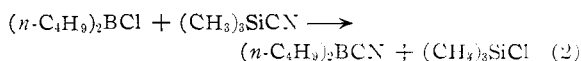
The new compound, $(n\text{-}C_4H_9)_2BCN$, may also be prepared conveniently by the metathetical reaction between di-n-butylboron chloride and silver cyanide. This method of preparation is similar to that used for the preparation of $B(OCN)_3$.[3]

Di-n-butylboron cyanide is a colorless, viscous liquid having a polymerization number of at least 20, judging by its cryoscopic behavior in benzene. The compound exhibits a well-defined C≡N

(1) This research was supported by the Office of Naval Research, Contract No. Nonr-551(21). Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) E. Charles Evers, W. O. Freitag, W. A. Kriner, J. N. Keith, A. G. MacDiarmid and S. Sujishi, This Journal, **81**, 4493 (1959).

(3) G. S. Forbes and H. H. Anderson, ibid., **62**, 761 (1940).

stretching frequency at 2280 cm.$^{-1}$, hence the cyanide group has not undergone any far reaching chemical transformation. Because of its polymeric nature it is not possible to designate the compound as either a normal or isocyanide since both the carbon and nitrogen atoms of each cyanide group are presumably attached to boron atoms.
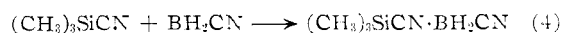
Depolymerization of the di-n-butylboron cyanide may be effected by ammonia. A fairly mobile, non-volatile liquid of empirical composition $(n\text{-}C_4H_9)_2BCN\cdot NH_3$ is obtained on removing excess ammonia at room temperature.

It appears very likely that a reversible ammonolysis might take place in liquid ammonia, viz.

$$(n\text{-}C_4H_9)_2BCN\cdot NH_3 + NH_3 \underset{\longleftarrow}{\overset{\longrightarrow}{}}$$
$$(n\text{-}C_4H_9)_2BNH_2 + NH_4CN \quad (3)$$

since treatment with sodium causes evolution of hydrogen and converts the cyanide to the corresponding monomeric amine, $(n\text{-}C_4H_9)_2BNH_2$, which previously has only been prepared in a more highly polymerized state.[4]

Just as NH_3 inhibits the polymerization of $(n\text{-}C_4H_9)_2BCN$ so also does $(CH_3)_3SiCN$ inhibit the polymerization of BH_2CN. When $(CH_3)_3SiCN\cdot BH_3$ is decomposed in the presence of $(CH_3)_3SiCN$, BH_2CN is not formed; instead there is produced $(CH_3)_3SiCN\cdot BH_2CN$, which is volatile at temperatures at which BH_2CN is completely involatile.[2] It therefore appears that the BH_2CN units, as formed, combine with $(CH_3)_3SiCN$ as indicated in equation 4 to form a monomeric material, instead of combining with themselves to form a polymer, viz.

$$(CH_3)_3SiCN + BH_2CN \longrightarrow (CH_3)_3SiCN\cdot BH_2CN \quad (4)$$

(4) R. B. Booth and C. A. Kraus, ibid., **74**, 1415 (1952).