sche Situation bezüglich des Zusammenhangs von Spinorkalkül und Bispinorkalkül hinsichtlich unserer Thematik aufzuklären. Außerdem ergaben sich Bedingungen, unter welchen der DIRACSche γ -Apparat in krummlinigen Koordinaten so formulierbar ist, daß gewissen Hermeizitätsforderungen entspro-

chen werden kann. Schließlich konnte der Weg genau verfolgt werden, wie sich die Axiomatik der PAULI-Matrizen in GALILEI-Koordinaten in den großen Rahmen einfügt.

Herrn NOTTROTT danke ich für Kontrollrechnungen.

NOTIZEN

On the C—N Stretching Frequencies in *para*-Substituted Anilines

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Many authors have shown that the stretching frequencies, the absorption intensities, and in some cases the band widths arising from vibrations localized in functional groups attached to an aromatic ring can be related to the electronic nature of the ring substituents through the HAMMETT substituent constants (σ)¹ based on chemical reactivity studies. Such correlations have been published for the OH stretching vibration in phenols², the C≡N stretching vibration in benzonitriles^{3–5}, the —NH stretching vibration in N-methyl anilines⁶, the NH₂ stretching vibrations in anilines^{5–8}, and the C=O stretching vibration in benzaldehydes⁹, ethyl benzoates⁹ and acetophenones^{9,10}. BROWN¹¹ has shown that in some cases such correlations are more appropriately made in terms of the electrophilic substituent constants σ^+ ¹². The high precision and accuracy of the recent infrared measurements in this field has justified a statistical treatment of the data by RAO and VENKATARAGHAVAN¹³.

Although such relations have contributed to our understanding of the structure and behaviour of organic molecules, they have remained largely empirical since completely satisfactory theoretical calculations of the substituent constants have not yet been made¹⁴. However, BROWN¹⁵ has shown, on the basis of a simple molecular orbital treatment, that such correlations of spectroscopic parameters with essentially kinetic constants are reasonable, since the changes in electron distribution which occur in the molecule during vibrational distortions closely parallel those which occur in the formation of the transition state during chemical reactions.

These correlations have also been shown to hold in such cases where the vibration involves one of the aromatic ring carbon atoms, as in the asymmetrical C—O—C stretching vibration in anisoles¹⁶. More recently RITSCHL¹⁷ has extended this to a simpler vibrational mode, the C—N stretching vibration in *para*-substituted anilines, where the frequency rises as the ring substituents become more electron withdrawing.

Since no interpretation was offered for this behaviour of the C—N stretching frequency, and since the NH₂ stretching vibrations in substituted anilines have been studied in great detail^{18,19}, it has now been possible to justify these results in a more fundamental manner. The HNH bond angle calculated from the NH₂ stretch-

¹ L. P. HAMMETT, *Physical Organic Chemistry*, McGraw-Hill, New York 1940, pp. 186 ff. Also see H. H. JAFFE, *Chem. Rev.* **53**, 191 [1953].

² P. J. STONE and H. W. THOMPSON, *Spectrochimica Acta* **10**, 17 [1957].

³ H. W. THOMPSON and G. STEEL, *Trans. Faraday Soc.* **52**, 1451 [1956].

⁴ M. F. A. E. SAYED, *J. Inorg. Nucl. Chem.* **10**, 168 [1959].

⁵ P. J. KRUEGER and H. W. THOMPSON, *Proc. Roy. Soc., Lond. A* **250**, 22 [1959].

⁶ P. J. KRUEGER and H. W. THOMPSON, *Proc. Roy. Soc., Lond. A* **243**, 143 [1957].

⁷ M. S. C. FLETT, *Trans. Faraday Soc.* **44**, 767 [1948].

⁸ S. CALIFANO and R. MOCCIA, *Gazz. Chim. Ital.* **86**, 1014 [1956].

⁹ H. W. THOMPSON, R. W. NEEDHAM and D. JAMESON, *Spectrochimica Acta* **9**, 208 [1957].

¹⁰ R. N. JONES, W. F. FORBES and W. A. MUELLER, *Canad. J. Chem.* **35**, 504 [1957].

¹¹ T. L. BROWN, *J. Amer. Chem. Soc.* **80**, 794 [1958].

¹² H. C. BROWN and Y. OKAMOTO, *J. Amer. Chem. Soc.* **79**, 1913 [1957]; *J. Org. Chem.* **22**, 485 [1957].

¹³ C. N. R. RAO and R. VENKATARAGHAVAN, *Canad. J. Chem.* **39**, 1757 [1961].

¹⁴ G. W. WHELAND, *Advanced Organic Chemistry*, 3rd edition, John Wiley & Sons, New York 1960, p. 535.

¹⁵ T. L. BROWN, *J. Phys. Chem.* **64**, 1798 [1960].

¹⁶ G. K. GOLDMAN, H. LEHMAN and C. N. R. RAO, *Canad. J. Chem.* **38**, 171 [1960].

¹⁷ F. RITSCHL, *Z. Chem.* **1**, 285 [1961].

¹⁸ P. J. KRUEGER, D. Phil. Thesis, Oxford University 1958.

¹⁹ P. J. KRUEGER, Comparative measurements on the fundamental and first overtone NH₂ stretching vibrations in dilute carbon tetrachloride solution for more than 60 *ortho*-, *meta*- and *para*-substituted anilines. To be published shortly.

ing frequencies²⁰ increases smoothly from 109.4° in *p*-phenylenediamine to 111.1° in aniline to 113.6° in *p*-nitroaniline, as the nitrogen atom changes from almost pure sp³ hybridization towards a state with a higher s/p ratio as the lone pair electrons are progressively delocalized over the aromatic ring. This increase in s-character is reflected in an increase in the NH₂ stretching frequencies, accompanied by a rise in the C—N stretching frequencies as this bond acquires more double bond character.

Quantitatively the constant *b*, which is the coefficient of the 2s-orbital of nitrogen in the hybrid²⁰

$$\psi_{\text{hybrid}} = b \psi_{2s} + \sqrt{1-b^2} \cdot \psi_{2p} \quad (1)$$

can be used as a measure of s-character of the hybrid nitrogen orbitals binding the hydrogen atoms. This coefficient can be calculated from the expression

$$b^2 = -\cos \Theta / (1 - \cos \Theta) \quad (2)$$

where Θ is the HNH angle. These results are tabulated in Table 1. Since *b* and the double-bond character of the C—N bond increase together as the substituent groups become more electron-withdrawing, a linear relationship between the C—N stretching force constant and *b* might be expected. In this closely related series of molecules this force constant should be proportional to the square of the corresponding stretching frequency. Fig. 1 shows that this linear dependence is observed.

²⁰ S. F. MASON, J. Chem. Soc. **1958**, 3619; see also J. W. LINNETT, Trans. Faraday Soc. **41**, 223 [1945].

Die Bildung von Cyclohexadienylradikalen durch Anlagerung von Wasserstoffatomen an festes Benzol

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In einer vorangehenden Arbeit¹ wurde das Elektronenspinresonanz (ESR)-Spektrum des bei 77 °K bestrahlten Benzols durch das Cyclohexadienylradikal interpretiert, das durch Anlagerung eines Wasserstoffatoms an den aromatischen Ring entsteht. Diese Interpretation ist auch von anderen Autoren² unabhängig von uns vorgeschlagen worden. Sie konnte weiterhin durch die Berechnung der Spindichtenverteilung des Radikals gestützt werden³, die gute Übereinstimmung zwischen dem Spektrum entnommenen „experimentellen“ und „theoretischen“ Werten ergab.

¹ H. FISCHER, Kolloid-Z. **180**, 64 [1962].

² W. A. TOLKATSCHEV, Y. N. MOLIN, J. J. CHKEIDZE, N. Y. BUBEN u. V. V. VOEVODSKIJ, Ber. Akad. Wiss. UdSSR **141**, 911 [1961].

Fig. 1. Relationship of the C—N stretching force constant in *para*-substituted anilines, as measured by the square of the corresponding stretching frequency, to the s-character of the hybrid nitrogen orbitals binding the hydrogen atoms. The abscissa axis also reflects an increase in the double-bond character of the C—N bond.

No.	Substituent	C—N Stretching Frequency (cm ⁻¹) ^a	s-Character ^b	HNH Angle (°) ^c
1	<i>p</i> -NH ₂ -	1261	0.499	109.4
2	<i>p</i> -CH ₃ O-	1270	0.504	109.9
3	<i>p</i> -CH ₃ -	1280	0.508	110.3
4	H-	1285	0.514	111.1
5	<i>p</i> -F-	1284	0.508	110.3
6	<i>p</i> -Cl-	1292	0.516	111.3
7	<i>p</i> -Br-	1290	0.521	111.8
8	<i>p</i> -I-	1290	0.525	112.4
9	<i>p</i> -NO ₂ -	1319	0.535	113.6

^a according to RITSCHL¹⁷; measurements in tetrahydrofuran.

^b calculated from equations (1) and (2), and equal to 0.500 for an sp³ hybrid orbital.

^c calculated from the symmetric and asymmetric NH₂ stretching frequencies according to LINNETT²⁰.

Table 1. The C—N Stretching Frequencies in *para*-Substituted Anilines.

Aus der Literatur⁴ ist nun bekannt, daß durch Anlagerung von Wasserstoffatomen an aromatische Verbindungen hydrierte Ringsysteme gebildet werden. Wenn diese Hydrierung nach einem Radikalmechanismus abläuft, sollten insbesondere bei Benzol Cyclohexadienylradikale als instabile Zwischenprodukte auftreten, die durch ESR-Untersuchungen nachgewiesen

Abb. 1. ESR-Spektrum von Produkten der Reaktion zwischen Wasserstoffatomen und festem Benzol. Meßtemperatur 210 °K.

³ H. FISCHER, Z. Naturforsch. **17 a**, 354 [1962]; J. Chem. Phys., im Druck.

⁴ K. H. GEIB u. P. HARTECK, Chem. Ber. **66**, 1815 [1933].