of HgClI, HgBrI, and HgI_2 as reaction products. The maximum rise in temperature does not take more than 2-3 min in all cases. It would be noted that very small amounts of iodine would be consumed in such a short time interval. This indicates that the reaction of iodine, at least on the surface of mercurous halide grains, is very fast. In order to have an idea about the exact amount of iodine needed to react with mercurous halides during this period, different amounts of iodine were added to a known amount of mercurous chloride and mercurous iodide and the rise in temperature was noted. The results are given in Figure 17.

The amount of iodine which reacts instantaneously with mercurous chloride and mercurous iodide can be approximately estimated from Figure 17. Knowing the amount of reactants consumed and the temperature rise, an approximate estimate of heat of reaction can be made. For the first step of reaction i, it is found to be 2.0 kcal/mole. It was found that when 0.6485 g of iodine was added to 6.0707 g of mercurous chloride, no iodine was left unreacted. The approximate value of the heat of dissociation of HgClI into mercuric chloride and mercuric iodide is estimated to be 0.2 kcal/mole. In a similar manner the approximate value of the heat of reaction for reactions ii and iii were estimated to be 3.9 and 1.23 kcal/mole, respectively.

At this stage it is pertinent to make a few remarks about the physics of the reactions. It is quite clear that electron transfer is not involved in the reactions in the solid state, since $E°$ for the following reaction would be -0.37 v.

$$Hg_2^{2+} + I_2 = 2Hg^{2+} + 2I^-$$

The above reaction would not be thermodynamically favored. Experiments show that above reaction does not occur in aqueous medium. The magnitude of energy changes in the reactions as estimated above show that some sort of weak interaction is involved. It may either be charge-transfer interaction or dipole-induced dipole interaction. The latter has recently been shown to be involved in the formation of picrates of naphthols.[3] Subsequent lattice rearrangement may lead to the formation of reaction products. The break of HgClI seems to involve the displacement of interpenetrating lattices of mercuric chloride and mercuric iodide, since the energy change in the process is very small.

Acknowledgment. Thanks are due to Dr. Y. N. Chaturvedi and Dr. P. S. Bassi for the help rendered during the preliminary studies. The support of the Indian Council of Scientific and Industrial Research is gratefully acknowledged. The authors are also thankful to Professor C. N. R. Rao, Indian Institute of Technology, Kanpur for providing facilities for spectral studies.

Protonation of Aromatic Hydrocarbon Dinegative Ions. A Thermodynamical Study of the Carbanions MH^-

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Contribution from the Laboratory for Physical Chemistry of the Free University and the Laboratory for Physical Chemistry, University of Amsterdam, Amsterdam, The Netherlands. *Received July 12, 1966*

Abstract: The disproportionation of the carbanions MH^- derived from anthracene, tetracene, pentacene, pyrene, perylene, and phenanthrene has been investigated. The experimental results point to the occurrence of the following disproportionation equilibria: $2MH^- \rightleftarrows MH_2 + M^{2-}$, for tetracene and pentacene; $2MH^- \rightleftarrows MH_2^- + M^-$, for phenanthrene; and $2MH^- \rightleftarrows MH_2^{2-} + M$, for pyrene and perylene. For the carbanion derived from anthracene no observable disproportionation was found. Except for the carbanion from phenanthrene the tendency toward disproportionation could be explained from a thermodynamical study based on experimental and semiempirical data.

In a previous paper[1] a study has been made of the protonation of the dinegative ions of some aromatic hydrocarbons. The primary reaction products formed are the carbanions MH^- (eq 1) as has been established

$$M^{2-} + H^+ \rightleftarrows MH^- \tag{1}$$

for naphthalene, anthracene, tetracene, and pyrene by a comparison of their absorption spectra with those of the corresponding carbonium ions MH^+. The present paper deals with the disproportionation of some carbanions MH^- into their dihydro product MH_2 and the dinegative ion M^{2-} (eq 2). Such a disproportionation

$$2MH^- \rightleftarrows MH_2 + M^{2-} \tag{2}$$

reaction may be followed by an electron transfer according to eq 3 provided the reduction potential of the

$$MH_2 + M^{2-} \rightleftarrows MH_2^- + M^- \tag{3}$$

mononegative ion M^- is lower than that of the dihydro product MH_2. When the first reduction potential of MH_2 and the second reduction potential of M differ sufficiently, even two electrons may be transferred.

$$M^{2-} + MH_2 \rightleftarrows M + MH_2^{2-} \tag{4}$$

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[1] N. H. Velthorst and G. J. Hoijtink, *J. Am. Chem. Soc.*, **87**, 4529 1965).

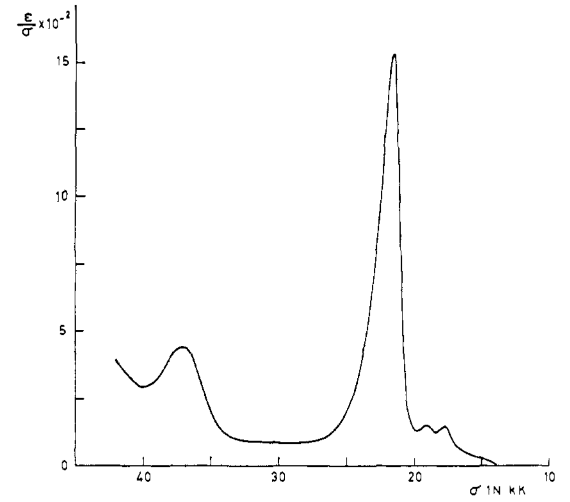

Figure 1. Electronic absorption spectrum of the dinegative ion of a dihydropyrene (presumably the 2,3-dihydro compound; see text).

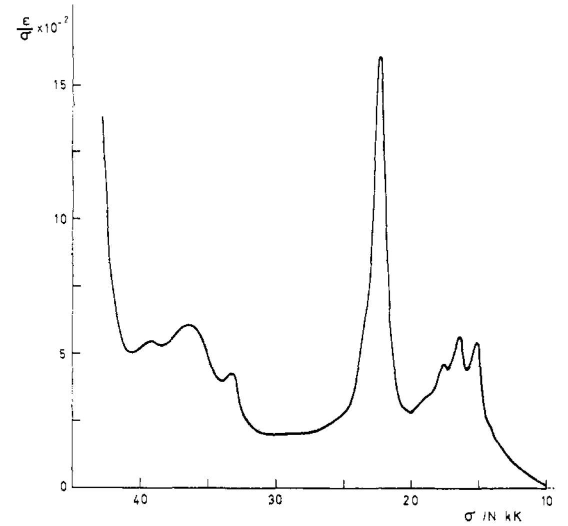

Figure 2. Electronic absorption spectrum of the dinegative ion of a dihydroperylene (presumably the 2,3-dihydro compound; see text).

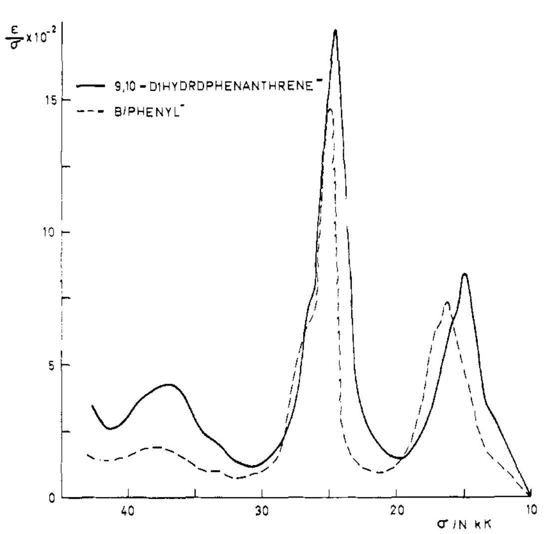

Figure 3. Electronic absorption spectra of the mononegative ions of biphenyl and 9,10-dihydrophenanthrene. The spectrum of the biphenyl mononegative ion is taken from *Mol. Phys.*, **7**, 1 (1963).

Experimental Section

The following aromatic hydrocarbons have been investigated: tetracene, pentacene, pyrene, perylene, and phenanthrene. A 10^{-4} *M* solution of the aromatic hydrocarbon in tetrahydrofuran was treated with alkali metal (Na or K) until complete reduction. The dinegative ions thus obtained were protonated, using as a proton donor either the corresponding dihydro compound or stearyl alcohol. For details concerning the spectral measurements see ref 2.

Discussion of the Experimental Results

Starting with tetracene a spectroscopic analysis shows that the corresponding carbanion 5-MH^- disproportionates according to eq 2. By varying the amount of 5,12-MH_2 or M^{2-} we were able to determine the disproportion constant.

$$K = \frac{(M^{2-})(MH_2)}{(MH^-)^2} = 16.2 \qquad (5)$$

In the case of pentacene we could not obtain any indication of the presence of the carbanion. The optical spectrum revealed only the spectra of the 6,13-dihydropentacene molecule and the pentacene dinegative ion. Hence we may conclude that for the carbanion derived from pentacene equilibrium 2 is practically completely shifted to the right.

For pyrene the following experiments have been carried out. On the addition of stearyl alcohol to a solution of the pyrene dinegative ion the blue color of the solution turns at once into red and within 0.5 hr the red color changes into orange. From the similarity between the spectrum of the red solution and the spectrum of the carbonium ion MH^+ of pyrene we concluded in our previous paper[1] that initially proton addition takes place in accordance with (1) and that the proton in the carbanion MH^- is attached to carbon atom 3. The spectrum of the orange solution displays among others the absorption of the pyrene molecule. From the extinctions measured we must conclude that half of the pyrene ion is converted into the pyrene molecule, which points to reaction 6. The electronic

$$2MH^- \rightleftarrows M + MH_2^{2-} \qquad (6)$$

absorption spectrum of the dinegative ion formed in reaction 6 is shown in Figure 1.

For perylene we found the following: On adding stearyl alcohol to a solution of the perylene dinegative ion (ratio 1:1) the violet solution changes into a blue-green solution. The results are similar to those obtained for pyrene. Hence we may again conclude that equilibrium 6 is practically completely shifted to the right. The electronic absorption spectrum of the dinegative ion obtained by disproportionation and electron transfer is given in Figure 2.

In the reaction between the phenanthrene dinegative ion and stearyl alcohol the formed products are the mononegative ion of 9,10-dihydrophenanthrene and the mononegative ion of phenanthrene itself. The structure of the dihydro derivative becomes immediately clear from a comparison between the spectrum of its mononegative ion and the spectrum of the mononegative ion of biphenyl (see Figure 3). The same results are obtained by the addition of 9,10-dihydrophenanthrene to a solution of the phenanthrene dinegative

(2) K. H. J. Buschow, J. Dieleman, and G. J. Hoijtink, *J. Chem. Phys.*, **42**, 1993 (1965).

Table I. Thermodynamic Data Used in Calculations[a]

Aromatic hydrocarbon	$-\epsilon_1^{\mathrm{red}}$[b]	$-\epsilon_2^{\mathrm{red}}$[b]	Carbon no.	Log K_B'[c]	$H_c(\mathrm{MH_2}) - H_c(\mathrm{M})$, kcal/mole[f]
Anthracene	*1.94*	*2.52*	9	*+3.5*	
9,10-Dihydroanthracene	3.47	3.87			*−51.9* (62.0)
Tetracene	*1.55*	*2.11*	5	*+5.2*	
5,12-Dihydrotetracene	2.47	2.79			*−54.9* (60.7)
Pentacene	1.41	1.67	6	+8.0	
6,13-Dihydropentacene	2.42	2.79			−55.4 (59.4)
Pyrene	*2.06*	*2.64*	4	−0.6[d]	
			3	*+1.5*	
4,5-Dihydropyrene	2.44	2.76			−57.7 (57.1)
2,3-Dihydropyrene	1.70	1.97			−50.9 (63.9)
Perylene	*1.67*	*2.12*	1	+3.8[e]	
			3	*+3.8*	
1,2-Dihydroperylene	1.86	2.13			−53.4 (61.4)
2,3-Dihydroperylene	1.32	1.55			−48.1 (66.7)
Phenanthrene	*2.51*	2.76	9	*−4.1*	
			1	*−4.1*	
			4	−5.9	
9,10-Dihydrophenanthrene	*2.63*	3.04			−57.5 (57.3)
1,2-Dihydrophenanthrene	2.15	2.45			−52.7 (62.1)
3,4-Dihydrophenanthrene	2.28	2.59			−52.4 (62.4)

[a] The figures in italics have been measured; the others have been derived from eq 12, 13, 14, and 18. [b] Taken from A. C. Aten, C. Büthker, and G. J. Hoijtink, *Trans. Faraday Soc.*, **55**, 324 (1959). The reduction potentials of solutions of biphenyl, phenanthrene, and 9,10-dihydrophenanthrene in N,N-dimethylformamide have not been published before. [c] Taken from ref 3. [d] We have estimated log K_B' for 4-pyrene from the measured log K_B' of 3-pyrene and the predicted difference in log K_B' values for 3- and 4-pyrene. [e] We have taken the same log K_B' value for 3- and 1-perylene, since Mackor, *et al.*, observed that a mixture of these carbonium ions is obtained in the reaction of perylene and hydrogen fluoride (G. Dallinga, E. L. Mackor, and A. A. Verryn Stuart, *Mol. Phys.*, **1**, 123 (1958)). [f] Taken from ref 7. The values within parentheses refer to the bond localization energies ΔE_1.

ion, clearly indicating that electron transfer and no proton transfer takes place. Hence protonation of the phenanthrene dinegative ion proceeds according to

$$2\mathrm{M}^{2-} + 2\mathrm{H}^+ \rightleftarrows \mathrm{MH_2}^- + \mathrm{M}^- \tag{7}$$

Thermodynamical Considerations

In order to explain the foregoing results we have attempted to make estimates of the equilibrium constants of the various disproportionation equilibria. For that purpose we have calculated the free enthalpies of these equilibria using the following cycles

$$\begin{array}{lcl}
\mathrm{M}^{2-} & \rightleftarrows & \mathrm{M}^- + \mathrm{e} \\
\mathrm{M}^- & \rightleftarrows & \mathrm{M} + \mathrm{e} \\
\mathrm{M} + \mathrm{H}^+ & \rightleftarrows & \mathrm{MH}^+ \\
\mathrm{MH}^+ + \mathrm{e} & \rightleftarrows & \mathrm{MH}\cdot \\
\mathrm{MH}\cdot + \mathrm{e} & \rightleftarrows & \mathrm{MH}^- \\
\hline
\mathrm{M}^{2-} + \mathrm{H}^+ & \rightleftarrows & \mathrm{MH}^-
\end{array} \tag{1}$$

$$\begin{aligned}
\Delta G &= \epsilon_{\mathrm{M}^-}{}^{\mathrm{red}}F \\
\Delta G &= \epsilon_{\mathrm{M}}{}^{\mathrm{red}}F \\
\Delta G &= -RT\ln K_B' \\
\Delta G &= -\epsilon_{\mathrm{MH}\cdot}{}^{\mathrm{ox}}F \\
\Delta G &= -\epsilon_{\mathrm{MH}\cdot}{}^{\mathrm{red}}F \\
\hline
\Delta G &= -RT\ln K_1 = (\epsilon_{\mathrm{M}^-}{}^{\mathrm{red}} + \epsilon_{\mathrm{M}}{}^{\mathrm{red}})F - \\
&\qquad RT\ln K_B' - (\epsilon_{\mathrm{MH}\cdot}{}^{\mathrm{ox}} + \epsilon_{\mathrm{MH}\cdot}{}^{\mathrm{red}})F
\end{aligned} \tag{8}$$

$$\begin{array}{lcl}
2\mathrm{MH}^- & \rightleftarrows & 2\mathrm{M}^{2-} + 2\mathrm{H}^+ \\
\mathrm{M}^{2-} & \rightleftarrows & \mathrm{M}^- + \mathrm{e} \\
\mathrm{M}^- & \rightleftarrows & \mathrm{M} + \mathrm{e} \\
\mathrm{M} + \mathrm{H_2} & \rightleftarrows & \mathrm{MH_2} \\
2\mathrm{H}^+ + 2\mathrm{e} & \rightleftarrows & \mathrm{H_2} \\
\hline
2\mathrm{MH}^- & \rightleftarrows & \mathrm{MH_2} + \mathrm{M}^{2-}
\end{array} \tag{2}$$

$$\begin{aligned}
\Delta G &= RT\ln K_1 \\
\Delta G &= \epsilon_{\mathrm{M}^-}{}^{\mathrm{red}}F \\
\Delta G &= \epsilon_{\mathrm{M}}{}^{\mathrm{red}}F \\
\Delta G &= \Delta G_{\mathrm{g}} + \Delta G_{\mathrm{solv}} \\
\Delta G &= \text{constant} \\
\hline
\Delta G_2 &= -RT\ln K_2 = 2RT\ln K_1 + (\epsilon_{\mathrm{M}^-}{}^{\mathrm{red}} + \\
&\qquad \epsilon_{\mathrm{M}}{}^{\mathrm{red}})F + \Delta G_{\mathrm{g}} + \Delta G_{\mathrm{solv}} + \text{constant}
\end{aligned} \tag{9}$$

$$\mathrm{MH_2} + \mathrm{M}^{2-} \rightleftarrows \mathrm{MH_2}^- + \mathrm{M}^- \tag{3}$$

$$\Delta G_3 = -RT\ln K_3 = (\epsilon_{\mathrm{M}^-}{}^{\mathrm{red}} - \epsilon_{\mathrm{MH_2}}{}^{\mathrm{red}})F \tag{10}$$

$$\mathrm{MH_2}^- + \mathrm{M}^- \rightleftarrows \mathrm{MH_2}^{2-} + \mathrm{M} \tag{4}$$

$$\Delta G_4 = -RT\ln K_4 = (\epsilon_{\mathrm{M}}{}^{\mathrm{red}} - \epsilon_{\mathrm{MH_2}^-}{}^{\mathrm{red}})F \tag{11}$$

Unfortunately we have not at our disposal the experimental values of all the quantities mentioned. The missing data however may be derived from the following relations. (a) Mackor, *et al.*,[3] measured the basicity constant K_B for various hydrocarbons and found a linear relation between $\log K_B' = \log K_B - \log z$ and the localization energy E_1

$$\log K_B' = 26.4E_1/\beta + \text{constant} \tag{12}$$

(z is the number of the equivalent positions in the aromatic hydrocarbon). The constant term in (12) may be determined from known K_B' and E_1 values and amounts to 56.7, so that unknown basicity constants may be derived from (12). This relation does not give correct values for *peri*-condensed compounds. In general these compounds are more basic than relation 12 predicts. In this case we followed a slightly different procedure (see text under Table I).

(b) For the unknown reduction potentials $\epsilon_{\mathrm{M}}{}^{\mathrm{red}}$ and $\epsilon_{\mathrm{M}^-}{}^{\mathrm{red}}$ we have made use of the semiempirical relations

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(3) E. L. Mackor, A. Hofstra, and J. H. van der Waals, *Trans. Faraday Soc.*, **54**, 66, 186 (1958).

$$\epsilon_1 = 2.54x_j - 0.85 \text{ v} \qquad (13)$$

$$\epsilon_2 = 2.82x_j - 1.05 \text{ v} \qquad (14)$$

in which ϵ_1 and ϵ_2 denote the first and second reduction potential, respectively, and x_j is the root of the Hückel secular determinant for the lowest antibonding π orbital.[4]

(c) Both in the scope of the Hückel approximation and Pople's SCF method eq 15 holds.[5] As the solvation energy for the ions MH^+ and MH^- may be considered to have practically the same value, it is reasonable to transfer eq 15 into

$$I + A = \text{constant} \qquad (15)$$

$$\epsilon_{MH\cdot}{}^{ox} + \epsilon_{MH\cdot}{}^{red} = \text{constant} \qquad (15a)$$

This relation has been shown to be valid also for even alternant hydrocarbon molecules.[6]

(d) ΔG_{solv} may be neglected as the reaction takes place between compounds which have no net positive or negative charge.

(e) ΔG_g may be replaced by

$$\Delta H_g - T\Delta S_g = \Delta H(MH_2) - \Delta H(M) - T\Delta S_g + \text{constant} \qquad (16)$$

in which $\Delta H(MH_2)$ and $\Delta H(M)$ are the heat of formation of MH_2 and M, respectively. ΔS_g is the entropy of hydrogenation in the gas state, which may be taken as a constant term for aromatic hydrocarbons in which steric effects do not occur.

As $\Delta H(MH_2) - \Delta H(M) = \Delta H_c(MH_2) - \Delta H_c(M) +$ constant, where $\Delta H_c(MH_2)$ and $\Delta H_c(M)$ are the heat of combustion of MH_2 and M, respectively, we may write

$$\Delta G_g = \Delta H_c(MH_2) - \Delta H_c(M) + \text{constant} \qquad (17)$$

In those cases where experimental data were not available we calculated the ΔG_g from the Hückel bond localization energies ΔE_l, as $\Delta H(MH_2) - \Delta H(M) = \Delta E_l$ + constant generally holds, and so

$$\Delta H_c(MH_2) - \Delta H_c(M) = \Delta E_l + \text{constant} \qquad (18)$$

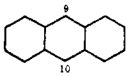
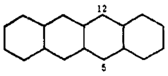
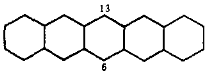
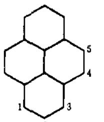
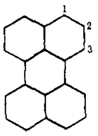
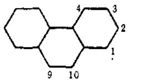
The missing constant term of eq 18 could be found by comparing the experimental known combustion data of M and MH_2 for anthracene and tetracene with the corresponding localization energies (the constant term equals −114.8 kcal).[7]

Discussion

On the basis of the eq 8, 9, 10, 11, 15a, and 18 and making use of the experimental and semiempirical data given in Table I, we calculated the equilibrium constants of reactions 2, 3, and 4. It is seen that eq 9 still contains an unknown constant. However, since the disproportionation constant of the carbanion derived from tetracene is known (5), we were able to derive a value for this constant (−45.1 kcal mole^{-1}).

In Table II the values for the equilibria constants are summarized. All partial reduction products MH_2 for which *a priori* it could be concluded that they would not participate in the disproportionation equilibrium have been left out of consideration (a criterion for this was the extremely unfavorable reduction potential of MH_2).

Table II. Estimated Equilibrium Constants for Disproportionations

Aromatic hydrocarbon	Carbon atom[a] MH^-	Carbon atom[a] MH_2	$2MH^- \rightleftarrows MH_2 + M^{2-}$ log K_2	$2MH^- \rightleftarrows MH_2^- + M^-$ log K_2K_3	$2MH^- \rightleftarrows MH_2^{2-} + M$ log $K_2K_3K_4$
	9	9, 10	−11	−27	−60
	5	5, 12	+1	−5	−26
	6	6, 13	+6	−7	−31
	4 3	4, 5 2, 3	−3 −12	0 +4	−12 +6
	1 3	1, 2 2, 3	+1 −3	+6 +11	−2 +13
	9 1 4	9, 10 1, 2 3, 4	−6 −10 −6	−4 +1 +2	−13 +2 +1

[a] To which a proton is attached.

The results shown in Table II lead to the following expectations. Anthracene-H⁻ is stable toward disproportionation, which agrees with the experimental results. Tetracene-H⁻ and pentacene-H⁻ disproportionate, giving the dinegative ion of the original aromatic molecule M^{2-} and a dihydro product MH_2. For pentacene-H⁻ equilibrium 2 is completely shifted to the right. This is in accordance with the experimental data.

Pyrene-H⁻ and perylene-H⁻ disproportionate practically completely according to reaction 6, giving the original molecule M and the dinegative ion of a dihydro product, MH^{2-}. From the experiments the same conclusion has been drawn. We have no experimental evidence for the structures of these dianions. On the basis of the semiempirical relations 13 and 14, however, we expect these ions to be the dinegative ions of 2,3-dihydropyrene and 2,3-dihydroperylene, respectively. So far the thermodynamical considerations seem to give a satisfactory explanation of the disproportionation of the carbanions MH^-. For phenanthrene, however, the thermodynamical predictions are in complete disagreement with the experimental results. Table II predicts the disproportionation of the carbanion derived from phenanthrene to lead to the negative ions of 1,2- or 3,4-dihydrophenanthrene and certainly not to the mononegative ion of 9,10-dihydrophenanthrene, as is found experimentally. For the moment we have no explanation for this divergent behavior.

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[4] G. J. Hoijtink, *Rec. Trav. Chim.*, **74**, 1525 (1955).

[5] N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, **51**, 600 (1955).

[6] G. J. Hoijtink, *Rec. Trav. Chim.*, **77**, 555 (1958).

[7] A. Magnus, H. Hartmann, and F. Becker, *Z. Physik. Chem.*, **197**, 75 (1951).