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DIARYLCARBENES OF UNUSUAL STERIC AND ELECTRONIC STRUCTURE

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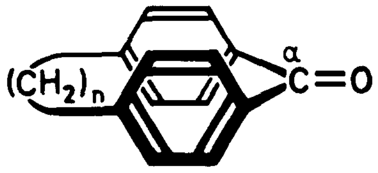
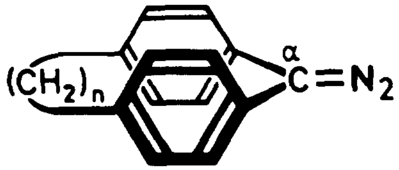
Abstract: Diarylcarbenes with the specific steric and electronic structure of [1.n]paracyclophanes (n = 8 - 12) were prepared and studied by ESR matrix investigations.

Recently Staab and Alt 1) reported the syntheses of α-oxo[1.n]paracyclophanes 1 (n = 8 - 12) and their hydrazones. These compounds were of interest as precursors of the diazo compounds 2 (n = 8 - 12) from which the carbenes 3a - e were to be prepared as diarylcarbenes with very unusual steric and electronic structure.

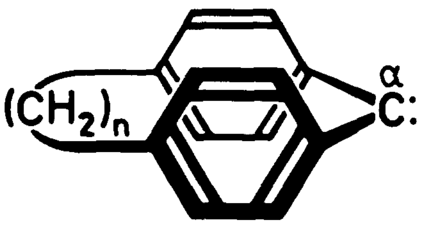


1a - e

	n
a	12
b	11
c	10
d	9
e	8



2a - e



3a - e

Diphenylcarbene, on the basis of experimental and theoretical evidence, is assumed to exist in the triplet ground state. The energy gap, however, between T_o and the first singlet state S_1 is expected to be rather small, and thermal equilibration $T_o \rightleftharpoons S_1$ is expected to be reached easily by intersystem crossing. Theoretical calculations predicted a different dependence of the energies of T_o and S_1 on the angle α between the two $C_{Ar}-C_{\alpha}$ bonds and on the torsional angles θ_1 and θ_2 by which the two aryl rings are twisted out of the central plane defined by the bonds on C_{α} 2,3). Metcalfe and Halevi 3) pointed out that for diarylcarbenes the singlet state might become more stable than the triplet state if the angle α is small and both aryl rings are twisted considerably relative to the central plane on C_{α}. Under these aspects the carbenes 3 are of considerable interest: From models it can be seen that in the whole series 3a to 3e the aryl rings relative to the α-plane are in a twisted configuration which with decreasing ring size is increasingly fixed in the perpendicular position ($\theta_1 = \theta_2 = 90^o$). Furthermore, in the same sequence the angle α becomes gradually smaller as is supported by experimental evidence for the analogous ketones 1 (IR, ^{13}C-NMR) 1). The carbene series 3a - e, therefore, seemed to be well suited to provide experimental evidence for the understanding of the structural factors determining the relative energies of spin states of diarylcarbenes. According to theoretical predictions especially the lower members of this series could be expected to be potential candidates for diarylcarbenes with singlet ground states.

From the hydrazones prepared from the α-oxo[1.n]paracyclophanes 1a - e 1) the corresponding diazo compounds 2a - e were obtained by oxidation (activated manganese dioxide, ether, 0°C). In the series from 2a to 2e a remarkable hypsochromic shift of the $n \rightarrow \pi^*$ absorption is observed [2a: λ_{max} = 518, 2b: 505, 2c: 495, 2d: 486, 2e: 455 nm; for reference, diphenyldiazomethane: 523 nm; all measurements in tetrachloromethane].

Solutions of 2a - e, as well as of diphenyldiazomethane as a standard, were prepared in paraffin oil ($c \sim 10^{-2}$ molar), degassed in quartz tubes under ice-cooling and sealed off. These tubes were placed in a quartz dewar adjusted into the cavity of an ESR spectrometer (Varian E-4) and cooled down to 93 K by a nitrogen stream obtained from liquid nitrogen by using an automatic temperature-control. When the temperature was constant the magnet was switched on and the sample was irradiated (200 W Hg superpressure lamp, filter Schott GG $\lambda > 395$ nm). Irradiation of 5 min was sufficient to obtain triplet signals for diphenylcarbene, 3a, 3b and 3d; the signal intensity reached a maximum after about 1 h irradiation. Carbenes formed proved to be rather resistant to further irradiation. When keeping the samples at 93 K after irradiation the signal intensity remained unchanged for several hours. Under the conditions mentioned no signals at all for the carbenes 3c and 3e were detected when irradiating 2c and 2e.

The evaluation of the triplet derivative ESR spectra followed the assignment of the signals given by Wasserman et al. 4) for diphenylcarbene. The zero-field splitting parameters D and E for diphenylcarbene obtained from our experiments (D = 0.4057 cm^{-1}, E = 0.0197 cm^{-1}) are in satisfactory agreement with data reported earlier (D = 0.4050 cm^{-1}, E = 0.0194 cm^{-1}) 5). The D and E values determined for the carbenes 3 are listed in the table.

	D [cm^{-1}]	E [cm^{-1}]
3a	0.4199	0.0214
3b	0.4290	0.0220
3c	no ESR signal detected	
3d	0.4787	0.0233
3e	no ESR signal detected	

Table. Zero-field Splitting Parameters D and E for the Triplet States of the Carbenes 3.

In comparison to diphenylcarbene the D-values of the carbenes 3 reveal a systematic increase with the reduction of angle α on C_α and with increasing fixation of the aryl rings in a perpendicular configuration to the C_α-plane.

In fact, the D-value found for 3d, to our knowledge, is the highest D-value observed so far for a diarylcarbene. Obviously, this reflects a high concentration of the triplet electrons on C_α due to the restricted delocalisation into the aromatic units which is a consequence of the [1.n]paracyclophane structure.

It is tempting to correlate the fact that for 3c and 3e triplet signals could not be detected by ESR to the prediction that singlet ground states are more likely to exist for the smaller members of the series 3a - e (see discussion above). It should be stated, however, that from the preliminary measurements at relatively high temperature reported here conclusions with regard to singlet or triplet ground states should not be drawn. More information on this problem as well as on the triplet-singlet gap are expected from measurements of temperature-dependent ESR at very low temperature which have been started.

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