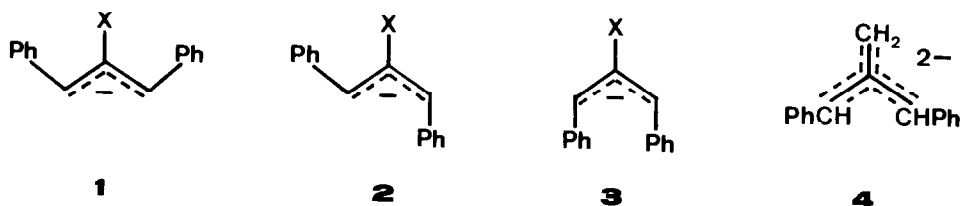


THE STEREOCHEMISTRY OF THE DIBENZYLIDENE-ETHYLENE DIANION

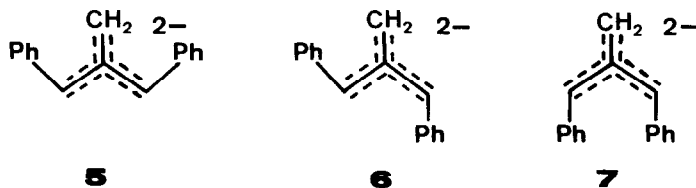
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Quench reactions, ^{13}C nmr spectra and MNDO molecular orbital calculations all suggest the title dianion to prefer the exo,exo-conformation, like the 1,3-diphenyl allyl anion, but in contrast to 2-substituted 1,3-diphenyl allyl anions.

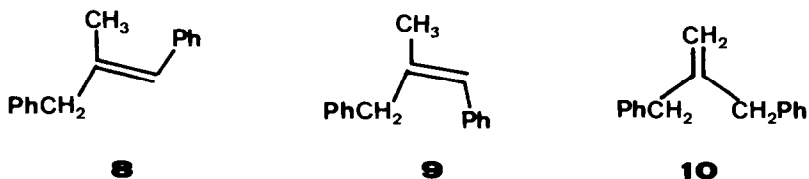
The stereochemistry of 1,3-diphenyl allyl anions has been extensively investigated.^{1,2} Only the parent anion with a hydrogen substituent at the 2-position is found to prefer the exo,exo-conformation 1.¹ Even a methyl substituent in the 2-position shifts the conformational equilibrium in favour of the exo,endo-isomer 2, and larger groups force the anion into the endo,endo-conformation 3.²



As part of our theoretical³ and experimental⁴ studies on γ -conjugated dianions we have now prepared the dibenzylidene-ethylene dianion 4 as the tetramethylethylenediamine (TMEDA) complex of its dilithium salt. Our results suggest that this dianion, which is a special example of a 2-substituted 1,3-diphenyl allyl anion, prefers the exo,exo-conformation 5, rather than exo,endo, 6, or endo,endo, 7.



Pure, orange crystals of 4 : 2Li^+ : 2 TMEDA can be obtained by reaction of the olefins 8-10 (obtained by dehydration of 1,1-dibenzyl ethanol) with two equivalents n-butyl lithium : TMEDA in hexane as described previously for the tribenzylidenemethane dianion.⁴



Reaction of these crystals with water at room temperature either as a slurry in hexane or in solution in benzene or THF gives predominantly the trans product 8. The product ratio (8:9:10) varies slightly with solvent, changing from 79:9:12 in hexane to 70:19:11 in THF. Quenching a THF solution or a pentane slurry with HCl gas at -90°C (conditions designed to avoid isomerisation of the intermediate allyl anions² or base-catalysed isomerization during the work-up) gives a product ratio of 80:5:15, showing that the high proportion of trans product 8 reflects the conformation of the original dianion.

We therefore conclude that 4 exists predominantly in the exo,exo-conformation 5. This conclusion is supported by ^1H and ^{13}C nmr. At room temperature in either C_6D_6 or THF-d_8 4 gives only seven ^{13}C peaks (see Fig. 1), indicating a structure of at least C_2 symmetry in which the phenyl rings are rotating (the two ortho and the two meta carbons in each ring are equivalent). Low temperature studies in THF-d_8 give a coalescence temperature for the ortho carbons of -35°C and a rotation barrier of 10.9 kcal/mol for the phenyl groups. This can be compared with a coalescence temperature of -60°C for the same process in the tribenzylidene-methane dianion salt.⁴ The ^1H spectrum remains unchanged from -70°C to room temperature. Although these results do not allow us to distinguish between 5 and 7, both of which have C_2 symmetry, we believe that the nmr and quenching experiments together indicate a large ($>95\%$) excess of the exo,exo isomer 5 in solution and in the solid state.

Finally, we have investigated the relative stabilities of 5, 6, and 7 using MNDO semi-empirical molecular orbital theory.⁵ 5 ($\Delta H_f = 104.8$ kcal/mol) is calculated to be significantly more stable than 6 or 7 ($\Delta H_f = 109.9$ and 109.6 kcal/mol, respectively). The MNDO calculated structure for 5 is shown in Fig. 2. The twisting of both the benzylidene and the phenyl groups out of plane is analogous to that found previously for the tribenzylidenemethane dianion⁴ and for the tetraphenyl cyclobutadiene dianion.⁶ The reason for the unexpected preference for the exo,exo-conformation is probably steric. Whereas allyl anions⁷ and allyl-alkali metal compounds⁸ have CCC angles around 130° , and therefore are very sensitive to interactions between exo substituents on the terminal carbons and bulky groups on C^2 , trimethylenemethane dianions have 120° CCC angles by symmetry. These angles can, however, be widened by steric interactions. The strain in 5 can be decreased by widening the $\text{C}^2\text{C}^1\text{C}^2$ angles to 122° . This process cannot take place as effectively in 6 as the two angle widenings work against each other. 7 is unfavourable as the $\text{C}^2\text{C}^1\text{C}^2$ angle cannot be widened enough to accommodate the two phenyl substituents. In 1,3-diphenyl allyl anions the large CCC angle makes the endo,endo conformer competitive in energy if the 2-substituent is large enough.²

ACKNOWLEDGMENTS

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Dr. E. Wilhelm for the nmr measurements and the staff of the Regionales Rechenzentrum Erlangen for their cooperation.

Fig. 1. ^{13}C spectrum of $\underline{4}$: 2Li^+ : 2TMEDA in THF-d_8 at 20°C . The carbon atoms are numbered as in Fig. 2. Chemical shifts are given in ppm relative to internal $(\text{CH}_3)_4\text{Si}$.

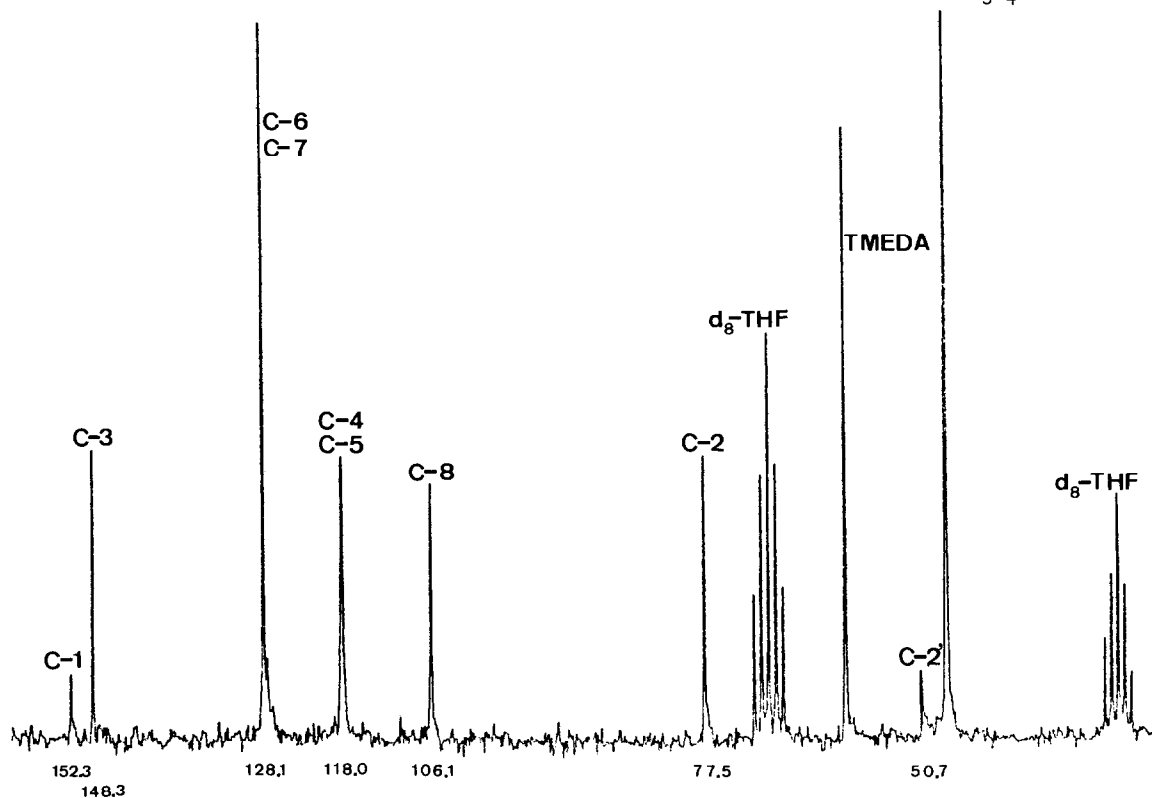
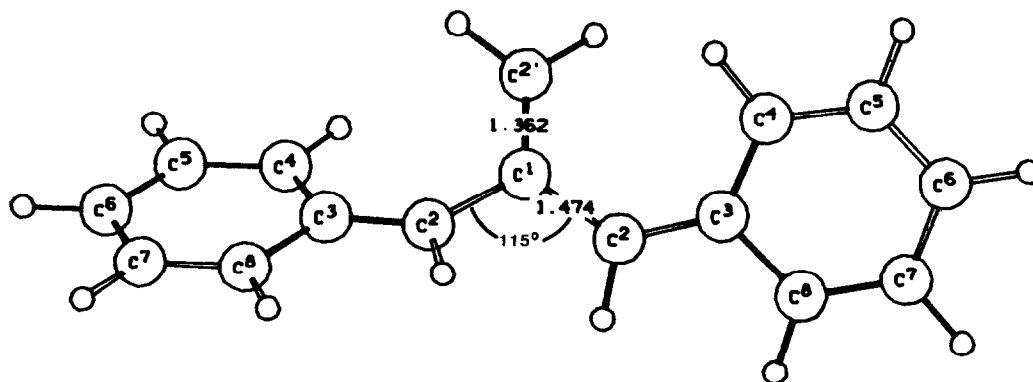


Fig. 2. MNDO optimised structure of $\underline{5}$ (calculated within C_2 symmetry). Bond angles are in degrees and bond lengths in Å.



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(Received in Germany 18 June 1983)