Y-Conjugated Dianions: a Comparison between the 1,1-Dibenzylethylene and Diphenylacetone-derived Dianions

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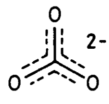
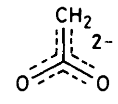
The lithium salts of the two title dianions have been synthesised and investigated by ^1H and ^{13}C n.m.r. spectroscopy. Whereas the dibenzylidenemethylenemethane dianion salt exists exclusively in the *exo,exo* conformation, its oxa-analogue is a mixture of two isomers, *exo,endo* and a symmetrical form, probably *exo,exo*. The benzyl α,β-CC bond rotation barrier in the ketone dianion salt in THF is 10.8 ± 0.5 kcal mol^{-1}. The phenyl rotation barrier in the hydrocarbon dianion salt is similar (10.9 kcal mol^{-1}), as are the charge distributions in the benzylidene groups of the two dianions.

A remarkably large number of Y-conjugated dianions are known. These include the parent members as well as derivatives of the entire series (1)—(4) obtained by substituting methylene groups for oxygens in the carbonate dianion.[1-10] The carbonate dianion (1) is certainly the most stable member of the series, but even the unsubstituted trimethylenemethane dianion (4), is remarkable in its ease of preparation.[9]

Our recent theoretical work [11] has suggested that the destabilizing electrostatic repulsion in Y-conjugated dianions and dications, in which the central carbon is practically neutral, is lower than in the corresponding cyclic Hückel aromatic compounds. This was demonstrated experimentally by using phenyl groups as probes to compare the charge distribution in the tribenzylidenemethane dianion [12] with that in the tetraphenylcyclobutadiene dianion.[13] We have now used the same strategy to evaluate the effect of replacing the methylene group of the dibenzylidenemethylenemethane dianion (5) by oxygen to give the diphenylacetone dianion (6). The effectiveness of the conjugation in these Y-conjugated dianions is our primary concern, but a comparison of the conformation of the dianions with 2-substituted 1,3-diphenylallyl anions is an additional concern.[14]



(1)



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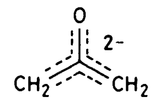

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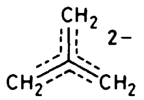

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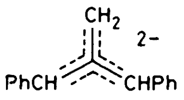

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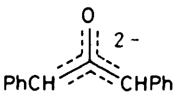


(6)

Table 1. Reaction products obtained from hydrolysis of (5) (Li^+–TMEDA)$_2$. Isolated yields were always greater than 95%. The proportions shown are relative to these yields

Solvent	Temperature °C	Quench reagent	(7)	(8)	(9)
Pentane [a]	20	H_2O	79	9	12
Pentane [a]	−90	HCl (gas)	80	5	15
THF	20	H_2O	70	19	11
THF	−90	HCl (gas)	82	10	8
THF	−90	10% H_2O–THF (slow addition)	67	31	2
Benzene	20	H_2O	75	18	7

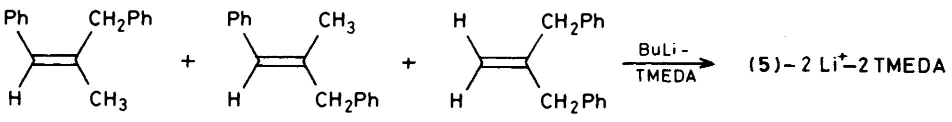
[a] Heterogeneous reaction mixture.

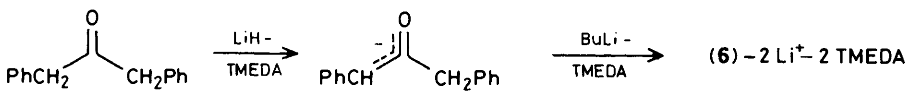
Results and Discussion

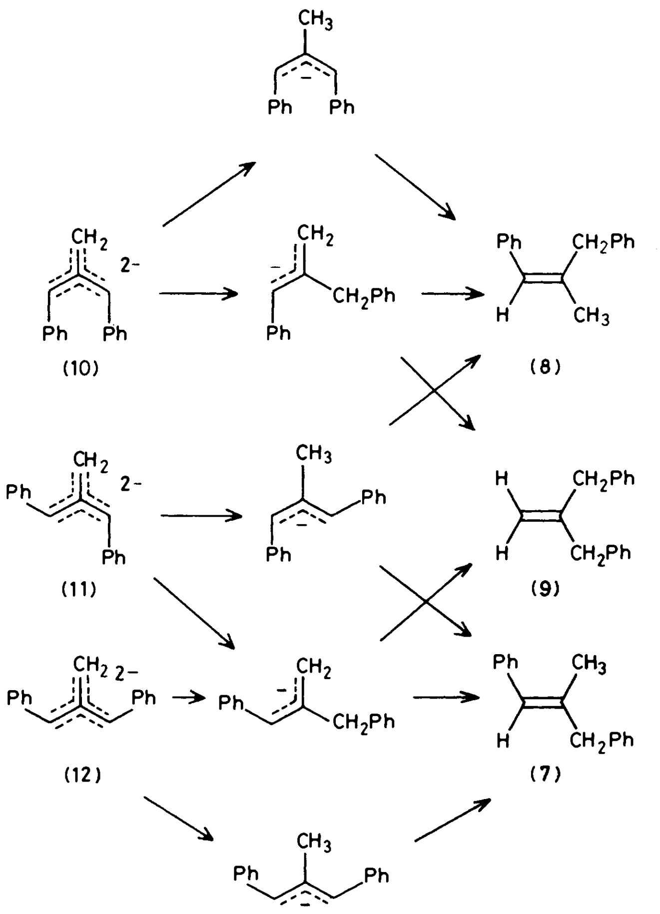
The dilithium salt of (5) was obtained as the crystalline adduct with two molecules of 2,5-diaza-2,5-dimethylhexane (TMEDA) directly from the metallation of the dehydration products of dibenzylmethylcarbinol [15] with two equivalents of n-butyl-lithium–TMEDA.

The dilithium salt of (6) was also obtained crystalline as an adduct with two TMEDA ligands. In this case, the preparation involved a stepwise metallation of dibenzyl ketone similar to those used previously for similar dianions.[7] However, in order to obtain the pure dilithium salt, lithium hydride was used as base with one equivalent of TMEDA. This combination is more effective than lithium hydride alone and gives a slow, but clean, deprotonation of the ketone to the lithium enolate, even in hexane solution. The second metallation was then carried out with BuLi–TMEDA. Both salts are soluble in THF and benzene.

Hydrolysis.—Quenching of (5) or (6) with D_2O gave dideuteriated products exclusively. Table 1 shows the products obtained from the hydrolysis of (5) (Li^+–TMEDA)$_2$ under various conditions. The reactions in pentane are heterogeneous. Low temperatures and non-polar solvents lead to larger, *trans* : *cis* (7) : (8) ratios, although the proportion of 1,1-dibenzylethylene (9) also varies between 7 and 15%. The main (70—82%) product is always the *trans*-isomer (7); this suggests a strong geometrical preference in the original dianion. Very slow addition of 10% water in THF to a solution at −90 °C gives products which approach the 53 : 47 : 0 ratio obtained on hydrolysis of 1,3-diphenyl-2-methylallyl-lithium.[14,16] The probable reaction sequence is shown in the Scheme. Assuming that the intermediate monoanion salt does not isomerise at low temperatures, as indicated by previous results,[14,16,17] and that fast quenching with HCl gas prevents subsequent base-catalysed isomerisation of the products, the reactions with HCl at −90°C should give a good indication of the stereochemistry of the dianion salt. As shown in the Scheme, our results can only be explained if (5) exists predominantly in the *exo,exo* conformation (10).[18] This conclusion contrasts with the behaviour of a series of 1,3-diphenylallyl anions. Only the parent (13; X = H), but none of the 2-substituted species show such a strong preference for the *exo,exo* conformation.[14] Even a methyl group in the 2-position (13; X = CH_3) shifts the conformation equilibrium in favour of the *exo,endo*-isomer



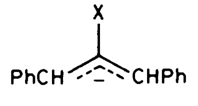




Scheme.

(68%). Increasing steric requirements of X lead to an increasing preference for *endo*-phenyl groups (see Table 2).

Table 2. Comparison of preferred conformations (%) of 2-substituted 1,3-diphenylallyl anion salts (13)



(13)

X	*exo,exo*	*exo,endo*	*endo,endo*
CH_2^- (5)	~100		
O^- (6)	35	65	
H [a]	~100		
CH_3 [a]	14	86	
C_2H_5 [a]	12	82	6
Ph [a]		72	28
Bu^t [a]			≥96

[a] Ref. 14.

^1H *N.m.r.*—The ^1H and ^{13}C n.m.r. spectra of (5)(Li^+–TMEDA)$_2$ in [$^2H_8$]THF are shown in Figure 1. Copies of the spectra at a range of temperatures are available on request. The benzylidene protons always appear as a single peak. This indicates either that the benzylidene groups are rotating fast even at −90 °C, or that the dianion exists in a single, symmetrical conformation over the entire temperature range. The former is unlikely as allyl anions have rotation barriers between 15 and 18 kcal mol^{-1} under these conditions.[14,16] Furthermore, the spectra show the onset of phenyl rotation at −60 °C, clearly; the barrier in THF is calculated [19] to be *ca.* 10.9 kcal mol^{-1} from the ^1H n.m.r. line shape analysis. It is unlikely that this barrier is larger than that for rotation of the benzylidene groups, so we conclude that a single, symmetrical isomer is probably present. The hydrolysis results discussed above suggest this to be the *exo,exo*-isomer, (10).

Figure 2 shows the ^1H and ^{13}C n.m.r. of (6) [$^2H_8$]THF at 20 °C. In contrast to (5), (6) shows two distinct stereoisomers at low temperatures, an unsymetrical species (65% at −80 °C) which must be the *exo,endo*-isomer (15) and a symmetrical species (35% at −80 °C) which is probably the *exo,exo*-rotamer (14). The *endo,endo*-isomer (16) is unlikely on the basis of the stereochemical preferences of (5) and of (13) with small 2-substituents, X.

The ^1H spectra yield an estimated barrier [19] of 10.6 kcal mol^{-1} for benzylidene rotation in (6). The phenyl rotation barrier must be similar, but cannot be determined clearly from the spectra.

^{13}C *N.m.r.*—The ^{13}C spectra of (5) (shown in Figure 1) show the same phenomena as the ^1H n.m.r. spectra. The phenyl rotation barrier is deduced [19] to be 10.9 kcal mol^{-1}, in good agreement with the value obtained from ^1H n.m.r. The charge distributions [20] (see Table 3) calculated from the chemical shifts show a similar degree of delocalisation to that found previously for dilithiotribenzylidenemethane.[12]

The ^{13}C spectra of (6) over a wide temperature range confirms the conclusions reached on the basis of ^1H n.m.r. The benzylidene rotation barrier determined [19] from the central carbon atom coalescence is 10.6 kcal mol^{-1}, and that from the benzylidene carbons 11.3 kcal mol^{-1}, giving a value of 10.8 ± 0.5 kcal mol^{-1} from one ^1H and two ^{13}C peaks. The charge distribution in the benzylidene groups (Table 3) is similar to that in (5).

I.r.—The double bond regions of the i.r. spectra of (5) and

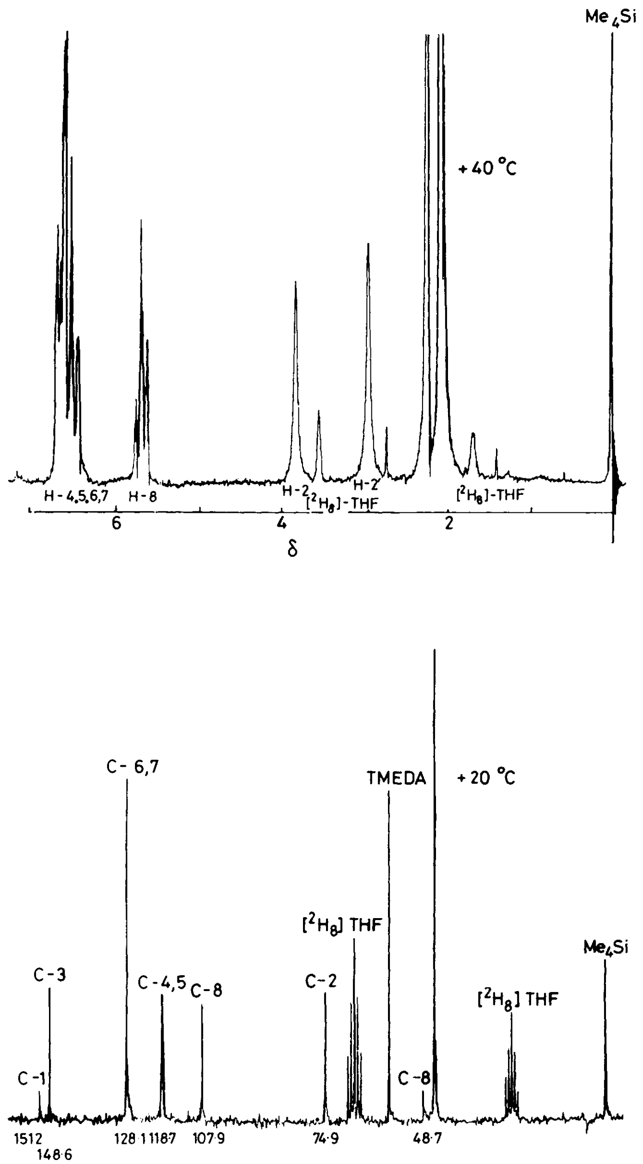


Figure 1. ^{1}H and ^{13}C n.m.r. spectra of (5)(Li$^+$-TMEDA)$_2$ in [^{2}H$_8$]THF

(6) in Nujol are shown in Figure 3. The C=C stretching frequency of (5) is 1 580 cm^{-1} and the C=O bond for (6) appears at 1 550 cm^{-1}. These values are compared with these for related species in Table 4.

Y-*Conjugation*.—The experimental data outlined above allow several independent assessments of the effectiveness of Y-conjugation.

The phenyl rotation barrier of 10.9 kcal mol^{-1} for (5) can be compared with 11.9 and 19 kcal mol^{-1} for the corresponding rotations in 1-phenylallyl-lithium [24] and in benzyl-lithium derivatives,[25] respectively. As the terminal carbon atoms in a trimethylenemethane dianion have a formal charge of $-2/3$, compared with $-1/2$ for the allyl anion and -1 for the methyl anion, a barrier of *ca.* 16 kcal mol^{-1} for (5) would be expected by interpolation. The barrier in the tribenzylidenemethane dianion [12] also is lower than expected. This suggests that conjugation to the phenyl groups in Y-aromatic dianions may be less important than in the reference phenylallyl and benzyl systems. Since the effects of the lithium atoms on the rotation barriers are not considered, this conclusion is tentative.

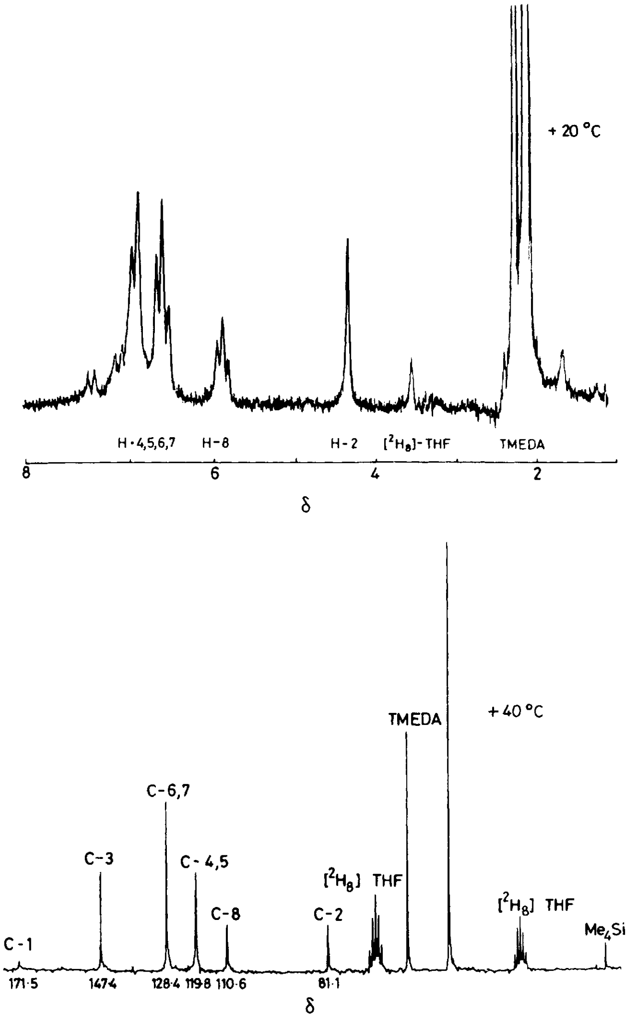


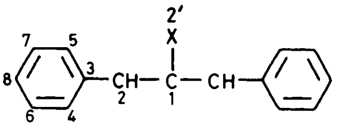
Figure 2. ^{1}H and ^{13}C n.m.r. spectra of (6)(Li$^+$-TMEDA)$_2$ in [^{2}H$_8$]THF

Similar reservations apply to any interpretation of the significance of the α,β-CC rotation barrier in (6), although the 10.8 kcal mol^{-1} value is reasonable when compared with known allyl-lithium rotation barriers.

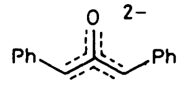
The charge densities derived from the ^{13}C chemical shifts [20] (Table 3) give values of -0.73 on each benzylidene group of (5), compared with -0.67 for (6). This is a surprisingly small difference in view of the electronegativities of carbon and oxygen, and suggests that Y-delocalisation is as effective in delocalising charge as normal phenyl conjugation. The C–O stretching frequency of (5) (Table 4) shows a weakening of the C–O bond in comparison with normal enolates, but the shift is not large, so that the C–O bond retains considerable double bond character. The i.r. spectrum of the trimethylenemethane dianion and other related species has been discussed by Sourisseau and Hervieu.[26] We conclude that the physical data of (5) and (6) are in agreement with a considerable degree of Y-conjugative stabilisation, which is also suggested by the relative ease of preparation of these species.

MNDO Calculations.—MNDO [27] optimised geometries and heats of formation for (10)—(12) and (14)—(16) are shown

Table 3. Comparison of MNDO calculated atomic charges with those derived from ^{13}C chemical shifts



X	1	2	2'	3	4	5	6	7	8
CH_2	0.12	−0.36	−0.54	0.09	−0.13	−0.08	−0.04	−0.03	−0.18
O	0.25	−0.34		0.09	−0.09		−0.04		−0.16
MNDO									
CH_2	0.11	−0.28	−0.23	0.09	−0.23	−0.21	0.00	0.00	−0.33
O	0.37	−0.37	−0.48	0.12	−0.24	−0.17	0.02	0.00	−0.31



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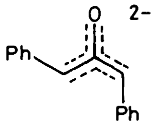

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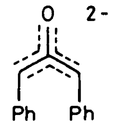

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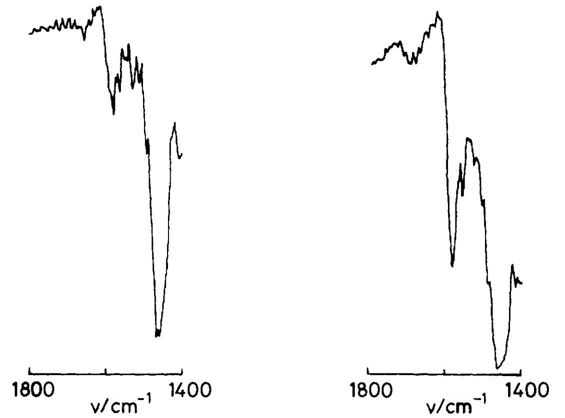
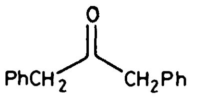


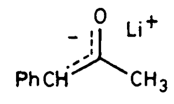
(5)(Li⁺-TMEDA)₂ (6)(Li⁺-TMEDA)₂

Figure 3. The double bond stretching regions of the i.r. spectra of (5) $(Li^+\text{-TMEDA})_2$ and (6)$(Li^+\text{-TMEDA})_2$ in Nujol

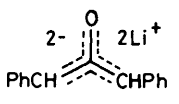
Table 4. Comparison of i.r. frequencies



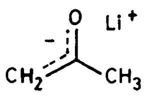
μ(CO) 1720 cm^{-1} (21)



1585 cm^{-1} (22)



1550 cm^{-1}



1610 cm^{-1} (23)

in Figure 4. For both (5) and (6), the *exo,exo*-conformations [(10) and (14), respectively] are found to be the most stable. This result agrees with our experimental findings for (5)-$(Li^+\text{-TMEDA})_2$, but not for (6)$(Li^+\text{-TMEDA})_2$, where the *exo,endo*-isomer (15) is preferred in solution. The trimethylenemethane dianion derivatives (10)—(12) have considerably shorter $C-CH_2$ than C–benzylidene bonds, indicating preferred localisation of charge on the phenyl-substituted carbons. This interpretation is confirmed by the charge densities (Table 3), but there are large deviations between experimental and calculated values. This was not the case for the tribenzylidenemethane dianion dilithium salt [12] and suggests either that MNDO is unable to correctly assess the electronegativity balance between methylene and benzylidene groups or that the charge distribution is perturbed by the lithium counter ions. In effect the MNDO calculations overestimate the importance of phenyl conjugation relative to delocalisation in the Y-system. The experimental results suggest a far larger negative charge on the methylene group, and hence more effective Y-conjugation. The dibenzylidene ketone dianion isomers (14)—(16) all have a short (*ca.* 1.25 Å) C=O bond, in agreement with the i.r. stretching frequency. The charge on each benzylidene group is −0.95, considerably higher than that obtained from the ^{13}C chemical shifts (see Table 3). As for the dibenzylidene-ethylene dianion the *para*-carbon atoms are calculated to be far too negatively charged.

Conclusions.—^1H and ^{13}C n.m.r. and i.r. studies indicate that the Y-delocalisation in the dianions (5) and (6) are both quite strong. Delocalisation to the methylene group in (5) is about as effective as that to the oxygen in (6).

Experimental

^1H, ^{13}C, and ^7Li n.m.r. spectra were measured with a JEOL PS-100 spectrometer, and i.r. spectra with a Beckmann IR12 instrument. All operations were carried out under argon or in a Braun MB200 glove box. TMEDA (Aldrich) was dried over calcium hydride.

Dibenzylidenemethylenemethane (5)$(Li^+\text{-TMEDA})_2$.—The salt was obtained crystalline in 82% yield direct from the metallation reaction mixture analogous to the tribenzylidenemethane dianion.[12]

Diphenylacetone Dianion Salt (6)$(Li^+\text{-TMEDA})_2$.—To a solution of dibenzyl ketone (4.2 g, 20 mmol; Aldrich) in hexane (300 ml), TMEDA (3.0 ml, 25 mmol) and lithium hydride (160 mg, 20 mmol) were added and the reaction stirred at room temperature for 24 h, followed by 6 days at reflux. The yellow solution was cooled to room temperature and further TMEDA (3.0 ml, 25 mmol) and n-butyllithium (12.5 ml, 1.6M) in hexane were added. The mixture was filtered after 15 min and the filtrate allowed to react at room temperature for 24 h. The dianion salt, which precipi-

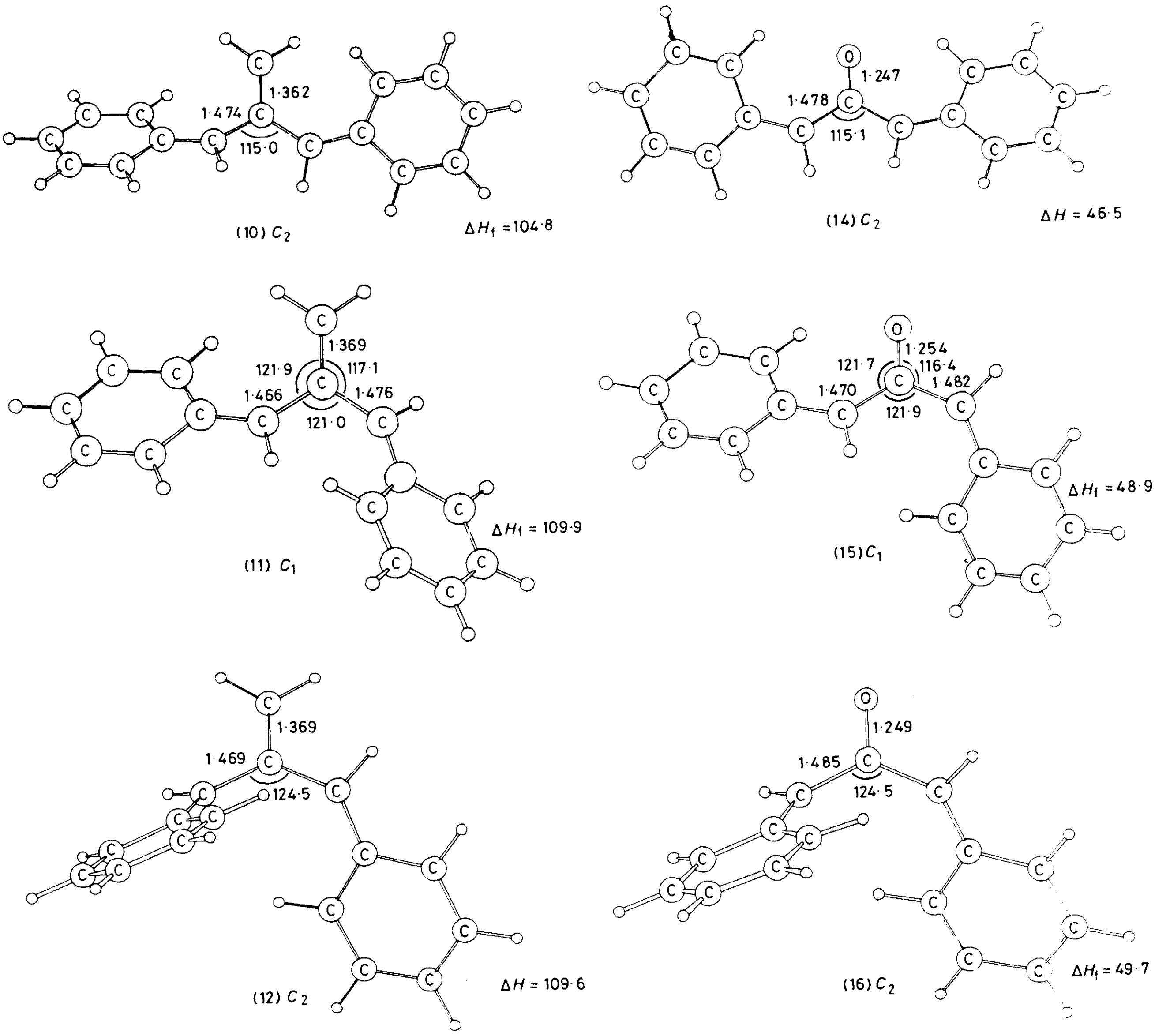


Figure 4. MNDO calculated structures of (10)—(12) and (14)—(16). Heats of formation are given in kcal mol^{-1}, bond lengths in Å, and angles in degrees

tated as a red powder (7.86 g, 87%), was filtered off and washed five times with pentane. Recrystallization from ether gave red-orange needles. Quenching with D_2O gave products which contained two deuterium atoms by ^1H n.m.r. and mass spectrometry for both (5) and (6).

We have now determined the X-ray structure of the ketone dianion salt (6).[28] The salt crystallizes in the *exo,exo*-form (14) and has a carbon–oxygen bond length of 1.33 Å. MNDO calculations [28] indicate that complexation with two lithium cations significantly lengthens the C–O bond relative to the dianion calculations reported here.

Acknowledgements

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