

46%. Components in the binary mixture of 11 and 12 were identified by comparison of spectral properties and GC retention times with those of authentic samples.³

Alkylation of (R)-(-)-3-OAc with Lithium *n*-Butylcyanocuprate. The pertinent results are presented in eq 2. The procedure for alkylation was the same as described above for alkylation of 2-OAc with LiCu(CN)CH₃, except that 2.6 M *n*-BuLi in *n*-hexane was used instead of ethereal MeLi. The isolated alkylation product had bp 85–86 °C (1.4 mm). The composition shown in eq 2 was determined by capillary GC as described earlier.⁶ Oxidation by the procedure described above for deter-

mination of the enantiomeric excess of active 4b gave (R)-(-)-7, [α]_D²² -12.3° (c 6, ether). Spectral properties were the same as for an authentic sample of *dl*-7.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE 8108535).

Registry No. (R)-(+)-2-OH, 62413-47-2; (R)-(+)-2-OAc, 84519-63-1; (R)-(-)-3-OH, 87246-95-5; (R)-(-)-3-OAc, 87246-94-4; (R)-(+)-6-OH, 22144-60-1; (R)-(+)-6-OAc, 84194-64-9; (R)-(-)-7, 51703-97-0; LiCu(*n*-Bu)₂, 24406-16-4; LiCu(CN)Me, 41753-78-0.

Further Examples of Enhanced Lengthening of Strained Carbon-Carbon Bonds by Orbital Interactions¹

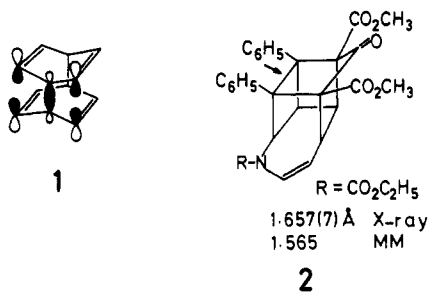
Eiji Ōsawa,* Petko M. Ivanov,^{2a} and Carlos Jaime^{2b}

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Received April 29, 1982

Three examples are given to supplement our previous observation of effective orbital interactions between π orbitals through a strained σ bond to give extraordinarily long C-C bonds. They are 3,5-disubstituted 2,6-diphenylpentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-4,8,11-trione (3b,c), pentacyclo[8.6.0.0^{1,5}.0^{2,9}.0^{6,11}]hexadeca-3,7,13,15-tetraene (4a), and *anti*-5,6-di-*n*-butyl-5,6-diphenyldecane (5a). One of the cyclobutane bonds in 3b,c and 4a, as well as the central bond of 5a, well exceeds 1.6 Å. The operation of the through-bond coupling between phenyl or vinyl groups in these molecules has been inferred from combined molecular mechanics and semiempirical MNDO molecular orbital calculations. Effects of para substituents in 1,4-diphenylbicyclo[2.2.0]hexane (7c) have been studied computationally by using the MNDO method, and π donor groups such as O⁻ and CO₂⁻ are found to further elongate the central bond up to 0.02 Å. Direct substitution of π donor groups at C₁ and C₄ of the bicyclo[2.2.0]hexane skeleton is predicted to be more effective in giving longer lengths for the C₁-C₄ bond. Strong steric interactions among alkyl side chains in 5 are analyzed.

Recently, Mislow and his collaborators³ proposed that when a C-C σ bond is surrounded by parallel π systems as in the central bond of 1,1',4,4'-biphenylene (1), the bond



is elongated as the result of "through-bond" orbital interactions.⁴ Among a number of orbital interaction modes,

two of them, $\pi_- \rightarrow \sigma^*$ and $\sigma \rightarrow \pi_+^*$, contribute to the bond elongation, the former by increasing antibonding character in the occupied orbital and the latter by donating bonding electrons to the unoccupied orbital (Figure 1). Quantitative perturbational molecular orbital treatment of orbital interactions in 1 indicates that the former type, $\pi_- \rightarrow \sigma^*$, is dominant, because of greater overlap between these orbitals than that between σ and π_+^* orbitals.^{3b} The elongated bond often exceeds 1.6 Å.

We have recently realized that a remarkably long C-C bond found in cage molecule 2 provides an interesting extension of Mislow's bond-elongation mechanism: when the intervening σ bond has some prestrain, the bond-lengthening effect is strongly enhanced.⁵ This finding

(1) Part 16 of the series "Application of Potential Energy Calculations to Organic Chemistry". Part 15: Ōsawa, E.; Musso, H. *Angew. Chem., Int. Ed. Engl.* 1983, 22, 1. Part 14: Ōsawa, E. *J. Comput. Chem.* 1982, 3, 400. Part 13: Ōsawa, E.; Musso, H. *Top. Stereochem.* 1982, 13, 117.

(2) (a) Hokkaido University Postdoctoral Fellow on leave of absence from the Institute of Organic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria. (b) Recipient of Postdoctoral Fellowship from Comissió Interdepartamental de Recerca i Innovació Tecnològica, Generalitat de Catalunya, Spain, 1981-1983.

(3) (a) Dougherty, D. A.; Hounshell, W. D.; Schlegel, H. B.; Bell, R. T.; Mislow, K. *Tetrahedron Lett.* 1976, 3479. (b) Dougherty, D. A.; Schlegel, H. B.; Mislow, K. *Tetrahedron* 1978, 34, 1441.

(4) (a) Paddon-Row, M. N. *Acc. Chem. Res.* 1982, 15, 245. (b) Verhoeven, J. W.; Pasman, P. *Tetrahedron* 1981, 37, 943. (c) Spanget-Larsen, J.; de Korschagen, C.; Eckert-Maksic, M.; Gleiter, R. *Helv. Chim. Acta* 1982, 65, 968. (d) Gleiter, R.; Gubernator, K. *Chem. Ber.* 1982, 115, 3811. (e) Lee, I.; Cheun, Y. G.; Yang, K. *J. Comput. Chem.* 1982, 3, 565. (f) Ohsaku, M.; Shigemi, S.; Murata, H.; Imamura, A. *Tetrahedron* 1981, 37, 297. (g) Imamura, A.; Ohsaku, M. *Ibid.* 1981, 37, 2191. (h) Ernst, L.; Eltamany, S.; Hopf, H. *J. Am. Chem. Soc.* 1982, 104, 299. (i) Spanget-Larsen, J.; Gleiter, R.; Paquette, L. A.; Carmody, M. J.; Degenhardt, C. R. *Theor. Chim. Acta* 1978, 50, 145. (j) Spanget-Larsen, J.; Gleiter, R.; Klein, G.; Doecke, W.; Paquette, L. A. *Chem. Ber.* 1980, 113, 2120. (k) Paquette, L. A.; James, D. R.; Klein, G. *J. Org. Chem.* 1978, 43, 1287. (l) Klein, G.; Paquette, L. A. *Ibid.* 1978, 43, 1293. (m) Paquette, L. A.; Carmody, M. J. *Ibid.* 1978, 43, 1299. (n) Martin, H.-D.; Eisenman, E.; Kunze, M.; Bonacic-Koutecky, V. *Chem. Ber.* 1980, 113, 1153.

(5) Harano, K.; Ban, T.; Yasuda, M.; Ōsawa, E.; Kanematsu, K. *J. Am. Chem. Soc.* 1981, 103, 2310.

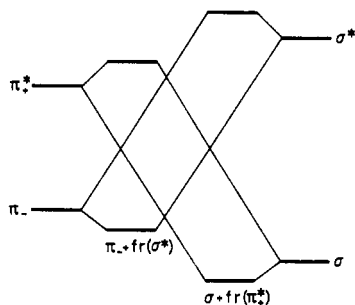
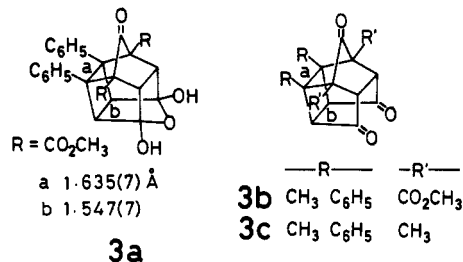


Figure 1. Schematic illustration of the two types of orbital interactions within **1** that cause the elongation of $C_{sp^2}-C_{sp^3}$ σ bonds. The $\pi \rightarrow \sigma^*$ interaction is dominant.

contrasts with the previous examples of bond elongation which have been confined to rather novel structures like **1**.^{3,6} The prospect of manipulating the length of C-C σ bond with such conventional substituents as the phenyl group appears to have great promise for both experimental and theoretical scrutiny. In this paper, we analyze several additional examples of very long C-C bonds which can also be attributed to the elongation by the "enhanced" through-bond mechanism and suggest some generality in the idea.

The first example (**3**)⁸ is related to **2** in that a cyclo-



butane ring constrained in a cage structure carries vicinal phenyl groups. As expected, the strained bond a of hydrate **3a** carrying two almost vertically oriented phenyl groups⁹ was found very long (1.635 ± 0.007 Å).⁸ We adopted the same strategy as used before^{3,7} to identify the operation of the through-bond interaction. Namely, if the interaction exists, the observed long bond will be underestimated by molecular mechanics but will be reproduced by molecular orbital calculations. If the Mulliken overlap population of the bond in question is increased by replacing the π substituent with a saturated one like methyl, the existence of through-bond interaction may be considered more likely. For the calculation we used triketones **3b**, which gave **3a** upon absorption of moisture.⁸ The length of bond a in **3b,c** (R = Ph) was grossly underestimated by molecular mechanics calculations (MM2)^{11,12} but was given a value close

Table I. Lengths and Overlap Populations of Strained C-C Bonds Carrying Vicinal Phenyl (Vinyl) or Methyl Groups as Calculated by Molecular Mechanics and MNDO^a

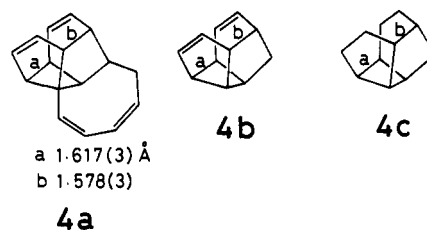
compd	bond length, ^b Å		Mulliken overlap population
	MM2 ^c	MNDO ^d	
3b (R = Ph)	1.5659	1.6229	0.9387
3b (R = Me)		(1.6229)	0.9979
3c (R = Ph)	1.5724	1.6265	0.9315
3c (R = Me)		(1.6265)	0.9930
4b (bond a)	1.5532	1.5893	0.9548
4c (bond a)		(1.5893)	1.1222
4b (bond b)	1.5460	1.5805	1.0324
4c (bond b)		(1.5805)	1.1044
5a	1.6148	1.6578 [1.634] ^e	0.9445
5b		(1.6578 [1.634] ^e)	0.9832
6a	1.5761		
6b	1.6114		
6c	1.6146		

^a In both MM2 and MNDO calculations, geometries were optimized for diphenyl (or diene) derivatives. These geometries were fixed for MNDO calculations of vicinal dimethyl (or saturated) derivatives. ^b Refers to the marked bond in the structure drawing. ^c Footnote 12. ^d Reference 13. ^e Corrected for branching error (see text).

to the X-ray value of **3a** by SCF-MO calculation with a MNDO approximation¹³ (Table I).¹⁴ The overlap population of this bond was increased significantly by replacing the phenyl group by methyl (**3b,c**, R = Me).¹⁵ Thus, the extra elongation of 0.09 Å in bond a of **3** relative to the molecular mechanics length can be attributed to the through-bond interaction.

The other bond b of **3b,c** is vicinally substituted with carbonyl groups fixed at a disposition favorable for the potential through-bond coupling. However, calculated lengths of bond b are in the normal range. Very small differences between the MM2 and MNDO values probably indicate a weak effect: **3b**, 1.5521 (MM2) and 1.5592 Å (MNDO); **3c**, 1.5496 (MM2) and 1.5585 Å (MNDO). This result is not surprising if one recalls the fact that the energy level of the occupied π orbital of the carbonyl group is generally much lower than that of π orbital of benzene.¹⁶ Larger energy separation between π and σ^* levels in ketones is expected to give poorer through-bond interaction. Conversely, if this interpretation is correct, it should be possible to increase the $\pi \rightarrow \sigma^*$ interaction by raising the energy level of the π orbital.¹⁷ This hypothesis is tested later in this paper.

A pentacyclic cage dimer of cyclooctatetraene (**4a**)¹⁸



(6) The effect of strain on the through-bond interaction has also been recognized by means of photoelectron^{1a,b} and electronic^{1c} spectra.

(7) (a) Gleiter, R.; Eckert-Maksic, M.; Schäfer, W.; Truesdale, E. A. *Chem. Ber.* **1982**, *115*, 2009. (b) Gleiter, R.; Gubernator, K.; Grimme, W. *J. Org. Chem.* **1981**, *46*, 1247. (c) Dewey, H. J.; Miller, R. D.; Michl, J. *J. Am. Chem. Soc.* **1982**, *104*, 5298.

(8) Okamoto, Y.; Harano, K.; Yasuda, M.; Ōsawa, E.; Kanematsu, K. *Chem. Pharm. Bull.* **1983**, *31*, 2526.

(9) ϕ_2^{10} : 73.3–107.3° according to Harano et al.⁸

(10) Hounshell, W. D.; Dougherty, D. A.; Hummel, J. P.; Mislow, K. *J. Am. Chem. Soc.* **1977**, *99*, 1916.

(11) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. (b) Allinger, N. L.; Yuh, Y. H. *QCPE* **1981**, *13*, 395.

(12) Aromatic carbon atoms were given a special natural bond length (1.3937 Å) and stretch force constant (8.0667 mdyne Å⁻¹). See also: (a) Beckhaus, H.-D. *Chem. Ber.* **1983**, *116*, 86. (b) Nachbar, R. B., Jr.; Hounshell, W. D.; Naman, V. A.; Wennerström, O.; Guenzi, A.; Mislow, K. *J. Org. Chem.* **1983**, *48*, 1227. (c) Ōsawa, E.; Onuki, Y.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 7475.

(13) (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. (b) *Ibid.*, **1977**, *99*, 4907. (c) Dewar, M. J. S.; Ford, G. P. *Ibid.* **1979**, *101*, 5558. (d) Thiel, W. *Ibid.* **1981**, *103*, 1413.

(14) According to MM2 and MNDO calculations, phenyl groups orient themselves in a virtually perpendicular disposition: calculated ϕ_2^{10} ranged between 75.4 and 90.5° for **3b,c**.

(15) Nuclear positions of methyl groups were optimized while the rest of molecule was fixed at the equilibrium geometry obtained with the diphenyl derivative.

(16) For example, compare the vertical ionization potentials of typical ketones and aldehydes (9.6–10.9 eV) with those of benzene (9.25 eV) or toluene (8.82 eV) (ref 13b, Table X).

(17) We thank a referee for this suggestion.

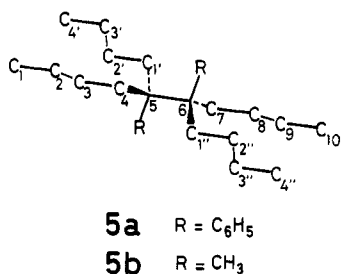
Table II. Lengths and Overlap Populations of Central C-C Bond and HOMO Energy Levels in 1,4-Disubstituted Bicyclo[2.2.0]hexanes (7) as Calculated by MNDO

	R	R'	HOMO, eV	C ₁ -C ₄ bond	
				length, Å	population ^a
7a ^b	H	H	-11.032	1.573 ^c	0.6222
7b ^b	CH ₃	CH ₃	-7.960	1.596	1.0115
7c ^b	C ₆ H ₅	C ₆ H ₅	-8.964	1.609	0.8819
7d	C ₆ H ₄ NH ₂ - <i>p</i>	C ₆ H ₄ NH ₂ - <i>p</i>	-8.408	1.611	0.9080
7e	C ₆ H ₄ -O ⁻ - <i>p</i>	C ₆ H ₄ -O ⁻ - <i>p</i>	-0.420	1.623	0.9166
7f	C ₆ H ₄ -CH ₂ ⁻ - <i>p</i>	C ₆ H ₄ -CH ₂ ⁻ - <i>p</i>	0.387	1.625	0.9226
7g	C ₆ H ₄ -O ⁻ - <i>p</i>	C ₆ H ₄ -NO ₂ - <i>p</i>	-3.231	1.632	0.9110
7h	O ⁻	O ⁻	2.843	1.638	0.6964
7i	CH ₂ ⁻	CH ₂ ⁻	4.304	1.657	0.7892
7j	O ⁻	NO ₂	-3.602	(2.828) ^d	(-0.0040) ^d
7k	O ⁻	CN ⁻	-2.466	(2.919) ^d	(-0.0032) ^d
7l	O ⁻	CO ₂ ⁻	0.583	1.669	0.4187

^a Mulliken bond overlap. ^b For MM2 calculations, see ref 5. ^c Experimental value of 1.577 (17) Å: Andersen, B.; Srinivasan, R. *Acta Chem. Scand.* 1972, 26, 3468-3474. ^d Cleaved bond.

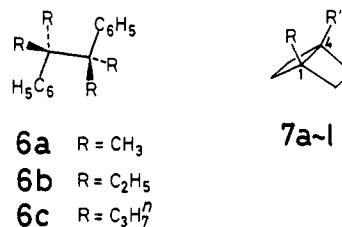
offers a unique situation for the straightforward detection of the prestrain effect. The coupling between juxtaposed double bonds in 4a can take place through bond a as well as through b. We would expect that the coupling will occur more strongly through the more strained bond a in the four-membered ring than through b in the five-membered ring. The observed¹⁸ lengths of these bonds indeed differ significantly in the expected direction. MM2 calculations of a model structure, 4b, showed that these bonds should have almost the same but smaller-than-the-observed lengths if steric effects alone are working (Table I). MNDO calculations reproduced the lengths almost perfectly for bond b and slightly less satisfactorily for bond a. The overlap population increased more in bond a than in b when the vinyl groups are saturated (4c, Table I).

An unusually long C-C bond recently discovered by Littke and Drück¹⁹ in a diphenylethane derivative, 5a



(1.638 ± 0.006 Å),²¹ is probably the first example of "enhanced" through-bond interactions in acyclic systems. Whereas 5a may appear just an ordinary branched alkane, it has a great prestrain around its central bond: MM2 calculations for 5a gave a very long central bond length of 1.61 Å (Table I).²⁰ The reason for the remarkable "mechanical" strain that led to the bond lengthening of up to 1.6 Å is the strong 1,5-nonbonded repulsions between C₃/C_{2'} and between C₈/C_{2'}, caused by g^F_g^M arrangement in C₃-C₄-C₅-C₁-C_{2'} and C₈-C₇-C₆-C₁'-C_{2'}, respectively, a forbidden conformation in *n*-pentane and similar to the Me/Me repulsion in 1,3-diaxial dimethylcyclohexane, which in turn intensifies gauche interactions across the central bond, causing its elongation.^{21,22} In order that this

strain be produced, the length of alkyl groups to be attached on the central ethane carbon atoms in 5 does not need to be as long as butyl; ethyl is large enough. Indeed, the MM2 central bond lengths of *anti*-1,2-diphenyl-1,1,2,2-tetraalkylethanes (6; alkyl = Me, Et, *n*-Pr) increased abruptly when methyls are replaced with ethyls (Table I).



Returning to 5, the rest of the elongation (1.64 - 1.61 = 0.03 Å) should then be ascribed to the orbital interaction between two phenyl groups through this strained central bond. MNDO calculations for 5a gave a central bond length of 1.6578 Å (Table I), which is considerably longer than the observed (1.638 Å), and this is probably related to the recent study of McManus²³ that indicates the tendency of MNDO (and of MINDO/3) to overestimate the C-C bond lengths of branched acyclic alkanes. According to McManus, the central bond length of hexamethylethane (1.582 ± 0.01 Å)²⁴ is calculated 1.606 Å by MNDO, the difference being 0.024 Å. If this overestimation is subtracted from the MNDO central length of 5a, one obtains 1.634 Å, which agrees well with the X-ray value. The MNDO overlap population of this bond behaved as expected upon replacement of the phenyls by methyls (5b).

Having observed the "prestrain" effect on the bond elongation in various structural types, we now look at the possibility of further enhancing the effect by increasing the energy of the occupied π MO level that interacts with the σ* orbital by introducing substituents. We chose 1,4-disubstituted bicyclo[2.2.0]hexane (7) as the model system, the central bond of which has been suggested to be sensitive to substitution at C₁ and C₄ with phenyl groups.⁵ While the introduction of 1,4-dimethyl groups (7b) lengthens the C₁-C₄ bond to some extent, phenyl groups (7c), which are sterically less demanding than

(18) Ōsawa, E.; Henke, H.; Schröder, G. *Tetrahedron Lett.* 1976, 847.

(19) Littke, W.; Drück, U. *Angew. Chem.* 1979, 91, 434.

(20) Littke and Drück¹⁹ note that molecular mechanics calculations of 5a by Beckhaus gave a length of 1.60 Å.

(21) Dale, J. "Stereochemistry and Conformational Analysis"; Verlag Chemie: New York, 1978; p 100.

(22) (a) Jaime, C.; Ōsawa, E. *J. Chem. Soc., Chem. Commun.* 1983, 708. (b) Jaime, C.; Ōsawa, E.; Takeuchi, Y.; Camps, P. *J. Org. Chem.*, in press. (c) Kane, V. V.; Martin, A. R.; Jaime, C.; Ōsawa, E., submitted for publication in *Tetrahedron*.

(23) McManus, S. P.; Smith, M. R.; Smith, M. B.; Shafer, S. G. *J. Comput. Chem.* 1980, 1, 233.

(24) Bartell, L. S.; Boates, T. L. *J. Mol. Struct.* 1976, 32, 379.

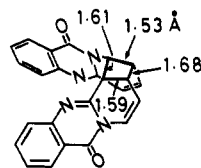
methyls, are more effective in the lengthening of the bond (Table II).

The HOMO π level of **7c** is increased by introducing π donor substituents like amino (**7d**) at the para positions of phenyl groups.²⁵ We realized that the groups carrying a negative charge like O⁻ (**7e**)^{25b} and CH₂⁻ (**7f**) are the most effective in this regard. MNDO calculations suggest that these para-substituted molecules will have a significantly longer central bond than **7c**, although the additional elongation due to the para substituent appears to be less than 0.02 Å. Interestingly the longest bond (1.632 Å) among the substituted phenyl derivative series presented in Table II is predicted for a "push-pull" type (**7g**) where one of the para substituents is not a dative but a captive group (nitro).

Since all the para substituents examined are capable of directly interacting with the σ orbital of the central bond, the phenyl group may be omitted. Attachment of these groups to C₁ and C₄ of bicyclo[2.2.0]hexane indeed proved more effective in elongating the central bond (**7h,i**). The push-pull type proved so effective that the central bond was broken during the energy minimization calculation when a nitro (**7j**) or cyano (**7k**) group was used as the captor group of the starting geometry. Compound **7l** gave the longest central bond (1.669 Å) in this series: the combination of O⁻ and CO₂⁻ comprises a weak push-pull system,²⁶ and O⁻ causes a π orbital with a very high energy level. These computational results remain to be tested experimentally.

The unusually long C-C bond should be reactive and hence useful to effect preferential cleavage.²⁷ Indeed, the long bond of **3a** has been shown to undergo rapid thermolysis.^{8,28} The long bond of **2** is particularly reactive: in addition to ready thermolysis,⁵ it readily cleaves upon electron transfer,²⁹ and upon treatment with various

metallic catalysts.³⁰ Zefirov³¹ reported that a photodimer (**8**) of 11*H*-pyrido[2,1-*b*]quinazolin-11-one is thermally



8

labile and readily undergoes [2 + 2] cyclofragmentation to give back the starting material in quantitative yield. X-ray analysis of **8**³¹ revealed that the cyclobutane ring contains very long C-C bonds in positions capable of effectively mediating the through-bond interaction between the two systems.³²

Acknowledgment. We thank Professors K. Kanematsu, K. Harano, K. Mislow, N. S. Zefirov, S. P. McManus, D. A. Dougherty, and E. D. Jemmis for helpful discussion and information. The work described herein was partially supported by a Grant-in-Aid from the Ministry of Education and by Kureha Chemical Industries Co. Calculations were carried out at the Computing Centers of Hokkaido University and of the Institute for Molecular Sciences.

Registry No. **3b** (R = Ph), 87136-20-7; **3b** (R = Me), 87136-21-8; **3c** (R = Ph), 65007-16-1; **3c** (R = Me), 87136-22-9; **4b**, 87136-23-0; **4c**, 87136-24-1; **5a**, 69961-18-8; **5b**, 87136-25-2; **6a**, 1889-67-4; **6b**, 62678-48-2; **6c**, 87136-26-3; **7a** (R = R' = H), 186-04-9; **7b** (R = R' = CH₃), 24322-10-9; **7c** (R = R' = C₆H₅), 77920-85-5; **7d** (R = R' = C₆H₄NH₂-*p*), 87136-27-4; **7e** (R = R' = C₆H₄O⁻-*p*), 87136-28-5; **7f** (R = R' = C₆H₄CH₂⁻-*p*), 87136-29-6; **7g** (R = C₆H₄O⁻-*p*; R' = C₆H₄NO₂-*p*), 87136-30-9; **7h** (R = R' = O⁻), 87136-31-0; **7i** (R = R' = CH₂⁻), 87136-32-1; **7j** (R = O⁻; R' = NO₂), 87136-33-2; **7k** (R = O⁻; R' = CN), 87136-34-3; **7l** (R = O⁻; R' = CO₂⁻), 87136-35-4.

(25) (a) Baker, A. D.; May, D. P.; Turner, D. W. *J. Chem. Soc. B* 1968, 22. (b) Pross, A.; Radom, L. *Prog. Phys. Org. Chem.* 1981, 13, 1. (c) Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. "Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules"; Halsted Press: New York, 1981.

(26) March, J. "Advanced Organic Chemistry"; McGraw-Hill: New York, 1968, p 241.

(27) Jones, P. G.; Kirby, A. J. *J. Chem. Soc., Chem. Commun.* 1979, 288.

(28) Mehta, G.; Srikrishna, A.; Reddy, A. V.; Nair, M. S. *Tetrahedron* 1981, 37, 4543.

(29) (a) Okada, K.; Hisamitsu, K.; Mukai, T. *J. Chem. Soc., Chem. Commun.* 1980, 941. (b) Mukai, T.; Sato, K.; Yamashita, Y. *J. Am. Chem. Soc.* 1981, 103, 670.

(30) Yokoyama, K.; et al. Paper Presented before the 45th Annual Conference of the Chemical Society of Japan, Tokyo, Japan, April 1982; Abstract 2F45.

(31) Zefirov, N. S.; Aslanov, L. A.; Rodes, L.; Yur'eva, N. M.; Trach, S. S.; Luzikov, Y. N.; Ionov, V. M.; Rybakov, V. B. *Zh. Org. Khim.* 1978, 14, 2407; *Chem. Abstr.* 1979, 90, 137762c.

(32) The extremely long bond length of 1.68 Å in **8** reported in ref 31 should be taken with some reservation in view of unsatisfactory quality of the crystal used (R factor 14.6%). The cell constants *a* and *b* reported in ref 31 should be interchanged (private communication from Professor Zefirov, April 2, 1982).