

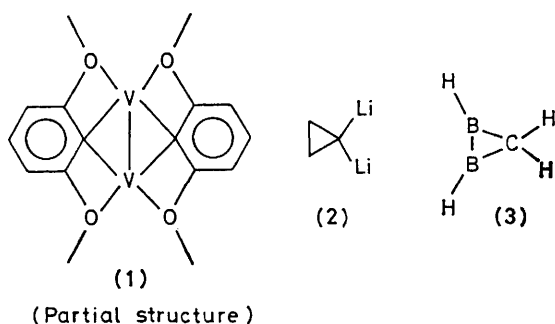
## Planar Tetraco-ordinate Carbon Candidates: MNDO Calculations on Substituted Phenyl-lithium Dimers

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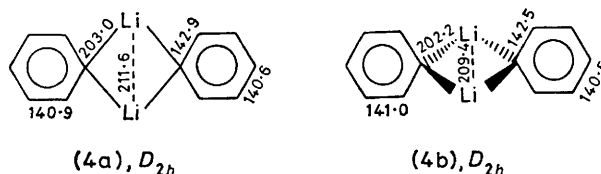
**Summary** MNDO calculations indicate the dimer of 2,6-dihydroxyphenyl-lithium (a model for the dimethoxy derivative) to prefer a geometry with two planar tetraco-ordinate carbon atoms; extended aromatic  $\pi$ -delocalisation, stability of multicentre  $\sigma$  bonds involving lithium, and 'intramolecular solvation' (chelation) are responsible for this preference.

THE vanadium complex (1) is the first structurally characterised compound with planar tetraco-ordinate carbon atoms.<sup>1</sup>



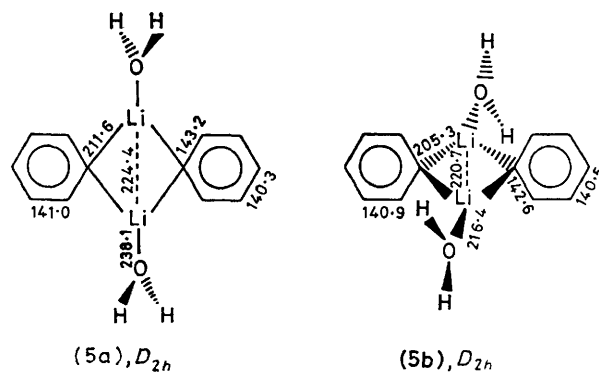
Reasons for this remarkable stereochemical preference are apparent; each planar tetraco-ordinate carbon atom is part of an aromatic system and is bound to two metals; these metals additionally are co-ordinated to the oxygen atoms of the *ortho*-methoxy substituents. We have emphasised the importance of the first two features in stabilising planar tetraco-ordinate carbon over tetrahedral alternatives.<sup>2</sup> Unlike tetrahedral carbon which forms four 2-centre 2-electron bonds, planar tetraco-ordinate carbon contains only six electrons in the  $\sigma$ -framework and has a lone pair of electrons in an MO with  $\pi$  symmetry. Substantial stabilisation is possible only if the substituents have a propensity not only to delocalise this lone pair, but also to participate in multicentre  $\sigma$ -bonding. Electropositive substituents are ideally suited for this purpose. The  $\pi$ -MO can be stabilised by the  $\pi$ -acceptor character of such substituents; involvement in an aromatic system is especially effective. Compounds (2) and (3), which have been calculated to prefer anti-van't Hoff geometries, are illustrative.<sup>2,3</sup>

Taking the hint provided by (1), we have now examined analogous, but simpler, systems computationally. Semi-empirical MNDO calculations<sup>4</sup> were first carried out on phenyl-lithium dimer.<sup>5</sup> The planar geometry (4a) ( $\Delta H_f^\circ = -141.0$  kJ mol<sup>-1</sup>) is calculated to be 24.7 kJ mol<sup>-1</sup> more stable than the 'tetrahedral' form (4b). The phenyl rings display aromatic bond lengths in both the planar (4a) and 'tetrahedral' (4b) geometries. The lithium atoms are bound to the carbons through 3-centre 2-electron bonds in both forms,<sup>6</sup> but such multicentre bonds are preferred in the planar structure (4a). Additionally, (4a) is stabilised by  $\pi$ -interaction between the vacant lithium orbitals and the occupied phenyl  $\pi$ -orbitals.

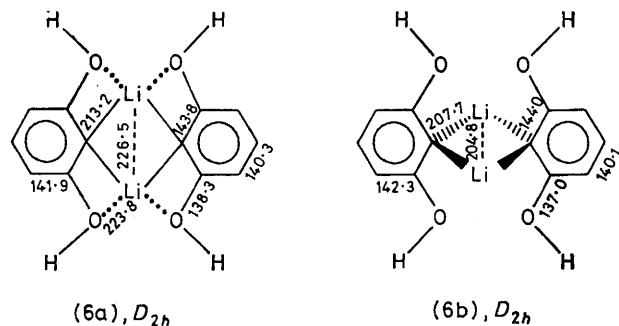


Bond lengths are given in pm in all the structures (4)–(6).

The X-ray structure of the tetramethylethylenediamine-complexed phenyl-lithium dimer, however, corresponds to tetrahedral co-ordination about C(1).<sup>7</sup> This change in stereochemistry is most likely due to solvent co-ordination to lithium which utilises the metal orbitals responsible for the preference for structure (4a). To confirm this hypothesis, calculations were carried out on model systems: phenyl-lithium dimers 'solvated' by the oxygen atoms of water molecules. Only two H<sub>2</sub>O molecules are enough to reverse the stability order of planar and tetrahedral forms. Tetrahedral (5b) ( $\Delta H_f^\circ = -725.4$  kJ mol<sup>-1</sup>) is 56.0 kJ mol<sup>-1</sup> more stable than planar (5a). Solvent co-ordinated lithium has reduced  $\sigma$ -donor and  $\pi$ -acceptor abilities and thus is less able to stabilise the planar tetraco-ordinate carbon geometries.



In the dimer of 2,6-dihydroxyphenyl-lithium (6), a model for the corresponding dimethoxy compound, the intrinsic preference of the phenyl-lithium dimer unit to adopt a planar geometry is reinforced through 'intramolecular solvation' (chelation). Planar (6a) is calculated to be convincingly more stable than tetrahedral (6b) ( $\Delta H_f^\circ = -942.1$  and  $-820.0$  kJ mol<sup>-1</sup>, respectively). The O–Li distance of 224 pm in (6a) is remarkably similar to the corresponding distances in H<sub>2</sub>O-co-ordinated phenyl-lithium dimer [238 pm in (5a), 216 pm in (5b)]. The geometry in (6a) must be nearly ideal for lithium–oxygen intramolecular chelation.<sup>8</sup> According to our calculations, additional co-ordination to two external H<sub>2</sub>O units does not increase the stability of this form. Tetrahedral (6b), on the other hand, profits significantly from the two additional H<sub>2</sub>O molecules. However, the 'internally solvated' (6a) remains the most stable geometry.



Although the present calculations are necessarily oversimplified in the treatment of solvent effects, some general principles are revealed. In addition to strain and to aromatic  $\pi$ - and multicentre  $\sigma$ -stabilisation,<sup>2</sup> a fourth effect, *viz.* intramolecular co-ordination, may be effective in producing a preference for planar tetraco-ordinate carbon geometries. Crystalline 2,6-dimethoxyphenyl-lithium and

similar intramolecularly chelated lithium derivatives are easily prepared.<sup>9</sup> X-Ray studies of such compounds are currently underway in our laboratories.<sup>10</sup>

These principles are not restricted to aryl-lithium dimers. Dimers of vinyl-lithium<sup>5</sup> with *cis*- $\beta$  electronegative substituents may adopt similar planar tetraco-ordinate carbon geometries. Fluoro, chloro, methoxy, and related vinyl-lithium derivatives, known experimentally,<sup>9,11</sup> deserve detailed structural investigation. Besides lithium and vanadium, other metals should function similarly. Rotation of aryl groups, through planar transition states possessing planar tetraco-ordinate carbon, has been observed experimentally in *o*-tolylcopper tetramer and in related  $Ar_4M_4$  and  $Ar_4M_2M'_2$  group 1B metal clusters.<sup>6</sup>

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<sup>1</sup> F. A. Cotton and M. Millar, *J. Am. Chem. Soc.*, 1977, **99**, 7886. The presence of planar tetraco-ordinate carbon atoms in (1) was first pointed out by R. Keese, R. Pfenninger, and A. Roesle, *Helv. Chim. Acta*, 1979, **62**, 326.

<sup>2</sup> J. B. Collins, J. D. Dill, E. D. Jemmis, P. v. R. Schleyer, R. Seeger, and J. A. Pople, *J. Am. Chem. Soc.*, 1976, **98**, 5419; K. Krogh-Jespersen, D. Cremer, D. Poppinger, J. A. Pople, P. v. R. Schleyer, and J. Chandrasekhar, *ibid.*, 1979, **101**, 4843; M. B. Krogh-Jespersen, J. Chandrasekhar, E.-U. Würthwein, J. B. Collins, and P. v. R. Schleyer, *ibid.*, 1980, **102**, 2263; J. Chandrasekhar, E.-U. Würthwein, and P. v. R. Schleyer, *Tetrahedron*, 1981, **36**, in the press. For an early discussion, see R. Hoffmann, R. W. Alder, and C. F. Wilcox, *J. Am. Chem. Soc.*, 1970, **92**, 4492; R. Hoffmann, *Pure Appl. Chem.*, 1971, **28**, 181.

<sup>3</sup> Although planar methane may be a singlet diradical (D. C. Crans and J. P. Snyder, *J. Am. Chem. Soc.*, 1980, **102**, 7152), closed shell singlets are likely for the highly  $\pi$ -stabilised species considered here.

<sup>4</sup> M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899; lithium parameterisation: W. Thiel and T. Clark, to be published.

<sup>5</sup> Phenyl-lithium is dimeric in ether solvents; for a review and discussion, see B. J. Wakefield, 'The Chemistry of Lithium Compounds,' Pergamon Press, Oxford, 1974, pp. 9-11. P. A. Scherr, R. J. Hogan, and J. P. Oliver, *J. Am. Chem. Soc.*, 1974, **96**, 6055, mention an INDO calculation on phenyl-lithium dimer.

<sup>6</sup> H. K. Hofstee, J. Boersma, and G. J. M. Van der Kerk, *J. Organomet. Chem.*, 1978, **144**, 255; G. Van Koten and J. G. Noltes, *ibid.*, 1979, **171**, C39; *J. Am. Chem. Soc.*, 1979, **101**, 6593; G. Van Koten, C. A. Shaap, J. T. B. H. Jastrzebski, and J. G. Noltes, *J. Organomet. Chem.*, 1980, **186**, 427.

<sup>7</sup> D. Thoennes and E. Weiss, *Chem. Ber.*, 1978, **111**, 3157.

<sup>8</sup> Model *ab initio* calculations by A. Pross and L. Radom, *Prog. Phys. Org. Chem.*, 1980, **13**, in the press, have shown that the HO..Li interaction in *o*-hydroxyphenyl-lithium monomer stabilises the system by 30 kJ mol<sup>-1</sup>. Dipole interaction and charge transfer are additional mechanisms for such stabilisation.

<sup>9</sup> U. Schöllkopf, 'Metallorganische Verbindungen,' Vol. XIII/1, p. 121, Houben-Weyl, G. Thieme Verlag, Stuttgart, 1970.

<sup>10</sup> W. Neugebauer, E. Wilhelm, and P. v. R. Schleyer, research in progress. *Added in proof:* The X-ray structure of 2,6-dimethoxyphenyl-lithium has just been published (H. Dietrich and D. Rewicki, *J. Organomet. Chem.*, 1981, **205**, 281). A hexamer with composition (C<sub>8</sub>H<sub>9</sub>O<sub>2</sub>Li)<sub>6</sub>Li<sub>2</sub>O was found whose structure unfortunately does not pertain to the possibilities discussed in the present paper.

<sup>11</sup> R. H. Wollenberg, K. F. Albizati, and R. Peries, *J. Am. Chem. Soc.*, 1977, **99**, 7365; L. Duhamel and J.-M. Poirier, *ibid.*, 1977, **99**, 8356; P. G. Gassman and I. Grennick, *ibid.*, 1980, **102**, 6863 and references cited therein.