

acidity in protonated purines. In contrast, electron-withdrawing groups are predicted to decrease N(7) basicity but promote C(8)H acidity of the protonated species II. N(7) protonation leaves substantial positive charge in the C(8)H regions. The magnitude of the charge in this region also appears to be directly related to the influence of groups at C(2) and C(6) in the purine system. Guanine, adenine, hypoxanthine, dimethyladenine, and dimethylguanine derivatives exhibit the strongest basicity (at N(7)) along with methyl- and methoxypurines. Xanthine and fluoro-, trifluoromethyl-, or nitropurine derivatives are computed to be among the weakest bases of the group. Ionization at C(8)H was predicted to be most facile for xanthine and fluoro-, trifluoromethyl-, and nitropurines and least facile for adenine, guanine, dimethylguanine, dimethyladenine, and hypoxanthine derivatives. The calculated results are in reasonably good agreement with experimental pK_a 's and isotope-exchange rate constants. Further refinement must await computations with inclusion of solvent and conformational effects from the ribofuranosyl ring and phosphate, an on-going project in our group. Finally, the proposed "ylide" intermediate III in the exchange reaction appears to retain zwitterionic character only in the σ -electron system. Considerable stabilization is achieved by polarization of the π -electron system.

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Registry No. I (R, Y = H, X = H), 120-73-0; I (R = Y = H, X = CH₃), 934-23-6; I (R, Y = H, X = NH₂), 452-06-2; I (R, Y = H, X = OCH₃), 37432-20-5; I (R, Y = H, X = OH), 95121-01-0; I (R, Y = H, X = COOCH₃), 95121-02-1; I (R, Y = H, X = OCF₃), 95121-03-2; I (R, Y = H, X = F), 1598-61-4; I (R, Y = H, X = CF₃), 95121-04-3; I (R, Y = H, X = CN), 95121-05-4; I (R, Y = H, X = NO₂), 95155-85-4; I (R, Y = H, X = O), 2308-57-8; I (R, Y = H, X = N(CH₃)₂), 37432-21-6; I (R, X = H, Y = CH₃), 2004-03-7; I (R, X = H, Y = NH₂), 73-24-5; I (R, X = H, Y = OMe), 1074-89-1; I (R, X = H, Y = OH), 95121-06-5; I (R, X = H, Y = COOMe), 62134-45-6; I (R, X = H, Y = OCF₃), 95121-07-6; I (R, X = H, Y = F), 1480-89-3; I (R, X = H, Y = CF₃), 2268-11-3; I (R, X = H, Y = CN), 2036-13-7; I (R, X = H, Y = NO₂), 95121-08-7; I (R, X = H, Y = O), 68-94-0; I (R, X = H, Y = N(CH₃)₂), 938-55-6; I (R = CH₂OH, X = H), 95121-09-8; I (R = CH₂OH, Y = H, X = CH₃), 95121-10-1; I (R = CH₂OH, Y = H, X = NH₂), 95121-11-2; I (R = CH₂OH, Y = H, X = OCH₃),

95121-12-3; I (R = CH₂OH, Y = H, X = OH), 95121-13-4; I (R = CH₂OH, Y = H, X = COOCH₃), 95121-14-5; I (R = CH₂OH, Y = H, X = OCF₃), 95121-15-6; I (R = CH₂OH, Y = H, X = F), 95121-16-7; I (R = CH₂OH, Y = H, X = CF₃), 95121-17-8; I (R = CH₂OH, Y = H, X = CN), 95121-18-9; I (R = CH₂OH, Y = H, X = NO₂), 95121-19-0; I (R = CH₂OH, Y = H, X = O), 95121-20-3; I (R = CH₂OH, Y = H, X = N(CH₃)₂), 95121-21-4; I (R = CH₂OH, X = H, Y = CH₃), 95121-22-5; I (R = CH₂OH, X = H, Y = NH₂), 95121-23-6; I (R = CH₂OH, X = H, Y = OCH₃), 95121-24-7; I (R = CH₂OH, X = H, Y = OH), 95121-25-8; I (R = CH₂OH, X = H, Y = COOCH₃), 95121-26-9; I (R = CH₂OH, X = H, Y = OCF₃), 95155-86-5; I (R = CH₂OH, X = H, Y = F), 95121-27-0; I (R = CH₂OH, X = H, Y = CF₃), 95121-28-1; I (R = CH₂OH, X = H, Y = CN), 95121-29-2; I (R = CH₂OH, X = H, Y = NO₂), 95121-30-5; I (R = CH₂OH, X = H, Y = O), 95121-31-6; I (R = CH₂OH, X = H, Y = N(CH₃)₂), 95121-32-7; II (R, Y = H, X = H), 18348-60-2; II (R, Y = H, X = CH₃), 95121-33-8; II (R, Y = H, X = NH₂), 58682-12-5; II (R, Y = H, X = OCH₃), 95121-34-9; II (R, Y = H, X = OH), 95121-35-0; II (R, Y = H, X = COOCH₃), 95121-36-1; II (R, Y = H, X = OCF₃), 95121-37-2; II (R, Y = H, X = F), 95121-38-3; II (R, Y = H, X = CF₃), 95121-39-4; II (R, Y = H, X = CN), 95121-40-7; II (R, Y = H, X = NO₂), 95121-41-8; II (R, Y = H, X = O), 95121-42-9; II (R, Y = H, X = N(CH₃)₂), 95121-43-0; II (R, X = H, Y = CH₃), 50291-79-7; II (R, X = H, Y = NH₂), 18444-01-4; II (R, X = H, Y = OCH₃), 95121-44-1; II (R, X = H, Y = OH), 95121-45-2; II (R, X = H, Y = COOCH₃), 95121-46-3; II (R, X = H, Y = OCF₃), 95121-47-4; II (R, X = H, Y = F), 95121-48-5; II (R, X = H, Y = CF₃), 95121-49-6; II (R, X = H, Y = CN), 95121-50-9; II (R, X = H, Y = NO₂), 95121-51-0; II (R, X = H, Y = O), 42007-36-3; II (R, X = H, Y = N(CH₃)₂), 80285-14-9; II (R = CH₂OH, Y = H, X = H), 95121-52-1; II (R = CH₂OH, Y = H, X = CH₃), 95121-53-2; II (R = CH₂OH, Y = H, X = NH₂), 95121-54-3; II (R = CH₂OH, Y = H, X = OCH₃), 95121-55-4; II (R = CH₂OH, Y = H, X = OH), 95121-56-5; II (R = CH₂OH, Y = H, X = COOCH₃), 95155-87-6; II (R = CH₂OH, Y = H, X = OCF₃), 95121-57-6; II (R = CH₂OH, Y = H, X = F), 95121-58-7; II (R = CH₂OH, Y = H, X = CF₃), 95121-59-8; II (R = CH₂OH, Y = H, X = CN), 95121-60-1; II (R = CH₂OH, Y = H, X = NO₂), 95121-61-2; II (R = CH₂OH, Y = H, X = O), 95121-62-3; II (R = CH₂OH, Y = H, X = N(CH₃)₂), 95121-63-4; II (R = CH₂OH, X = H, Y = CH₃), 95121-64-5; II (R = CH₂OH, X = H, Y = NH₂), 95121-65-6; II (R = CH₂OH, X = H, Y = OCH₃), 95121-66-7; II (R = CH₂OH, X = H, Y = OH), 95121-67-8; II (R = CH₂OH, X = H, Y = COOCH₃), 95121-68-9; II (R = CH₂OH, X = H, Y = OCF₃), 95121-69-0; II (R = CH₂OH, X = H, Y = F), 95121-70-3; II (R = CH₂OH, X = H, Y = CF₃), 95121-71-4; II (R = CH₂OH, X = H, Y = CN), 95121-72-5; II (R = CH₂OH, X = H, Y = NO₂), 95121-73-6; II (R = CH₂OH, X = H, Y = O), 95121-74-7; II (R = CH₂OH, X = H, Y = N(CH₃)₂), 95121-75-8.

Communications to the Editor

Structure of Dilithium Tetraphenylallene

Andrzej Rajca*[†] and Laren M. Tolbert*

Department of Chemistry, University of Kentucky
Lexington, Kentucky 40506

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The way in which a molecular framework distorts to accommodate negative charge provides a valuable reference point for comparison of experiment and theory.¹ Allene, for instance, which has two degenerate orthogonal π^* orbitals, can accommodate two

extra electrons in three limiting structures of C_{2v} , D_{2h}^{2a} and D_{2d} symmetry. The C_{2v} structure is distinguished from its "linear" counterparts by sp^2 rather than sp hybridization of the central carbon. Recent ab initio calculations of a model "dianion", 2,3-dilithiopropene, predict quasi- C_{2v} symmetry for the hydrocarbon framework and, further, give two energy minima for disposition of the lithium atoms, with a slight preference for a structure of C_s symmetry.^{2b} We now present definitive evidence that, for a tetraphenyl derivative of allene dianion, the actual structure is of C_2 symmetry, and we suggest that a structure involving lithium atoms bridging the C(1)-C(2) and C(2)-C(3) bonds coincides with the nuclear magnetic resonance data.

2,3-Dimetall-1,1,3,3-tetraphenylpropene has been postulated as an intermediate in the reduction of tetraphenylallene with alkali metals in diethyl ether, although the experimental evidence is

[†] On leave from the Technical University of Wroclaw, Wroclaw, Poland.
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(2) (a) The cation-free dianion $C_3H_2^{2-}$ was found to be a planar, linear D_{2h} species by MNDO calculations: Schleyer, P. v. R.; Kos, A. *J. Chem. Soc., Chem Commun.* **1982**, 448. (b) Kost, D.; Klein, J.; Streitwieser, A., Jr.; Schriver, G. W. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 3922.

Table I

compound ^a ¹³ C ₃	temp, °C		C(1) ppm	C(2) ppm	C(3) ppm	¹ J ₁₂ , Hz	¹ J ₂₃ , Hz	² J ₁₃ , Hz	ref (ppm relative to Me ₄ Si = 0.0 ppm)
1	-82	THF	118.1	205		40.0			THF, 67.96 ppm
2	+35	CDCl ₃	141.6	131.0	50.5	74.3	44.1	-1.1	Me ₄ Si, 0.0 ppm
3	-84	THF	113.5	209.4		103.3			THF, 67.96 ppm
4	-83	THF	105.7	132.6		67.8			THF, 67.96 ppm

^a Ph₂C=C=CPh₂²⁻, Li₂ (1), Ph₂C=CHCHPh₂ (2), Ph₂C=C=CPh₂ (3), Ph₂C=CHC(Li)Ph₂ (4).

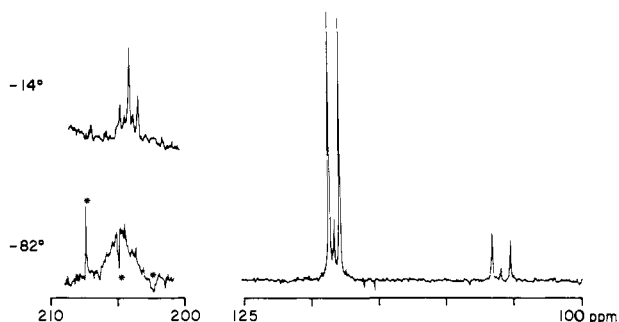


Figure 1. ¹³C NMR spectra of Ph₂CCCPh₂-¹³C₃, ⁷Li₂. The peaks labeled with * represent instrument noise.

tenuous.³ For instance, deuterium oxide quenching of the reaction mixture from reduction of the allene with sodium in diethyl ether at -78 °C produced the dideuterated propene in only 10% yield as opposed to 90% of the monodeuterated material.^{3a} Since the one-bond ¹³C-¹³C coupling constant (¹J(CC)) is generally accepted as a measure of the s character in the associated atomic orbitals,⁴ direct observation of the ¹³C NMR spectrum of triply enriched tetraphenylallene dianion appeared to be the method of choice both for establishing the existence of the species and determining its structure. Thus we now report generation of dilithium tetraphenylallene (1-Li₂) in >80% yield and its characterization by ¹³C and ⁶Li NMR.

Reaction of tetraphenylallene with lithium in tetrahydrofuran at -78 °C yielded, after quenching with methanol, 1,1,3,3-tetraphenylpropene (2)³ (93%). When a similar reaction mixture was quenched after 20 h with methanol-*d* a mixture of dideuterated (2-*d*₂) (82%) and the monodeuterated tetraphenylpropene (2-*d*) (18%) was isolated.

With tetraphenylallene-¹³C₃ (3)⁵ as a substrate reduction with lithium (natural abundance, 95.6% ⁷Li) in tetrahydrofuran (33% *d*₈) in a sealed 10-mm NMR tube in a -74 °C ultrasonic bath for 5 h afforded the ¹³C NMR spectrum shown in Figure 1. That the upfield doublet (δ 105.7, *J* = 67.8 Hz) was due to C(1) and C(3) of [1,1,3,3-tetraphenyl(allyl-¹³C₃)]lithium (4) (formed by protonation of the "dianion" 1) was confirmed by independent generation of 4 using 1,1,3,3-tetraphenylpropene-¹³C₃ (2-¹³C₃)⁶ and methyl lithium in tetrahydrofuran (Table I). The remaining signals in Figure 1 were assigned to the "dianion" 1, i.e., the downfield broad peak arises from the central carbon C(2) and the doublet (*J* = 40.0 Hz) arises from the terminal carbons. There are several characteristic features of the ¹³C NMR spectra of the

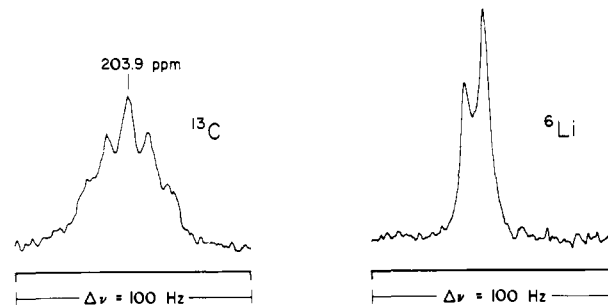


Figure 2. ¹³C and ⁶Li NMR spectra of Ph₂CCCPh₂-2-¹³C₃, ⁶Li₂.

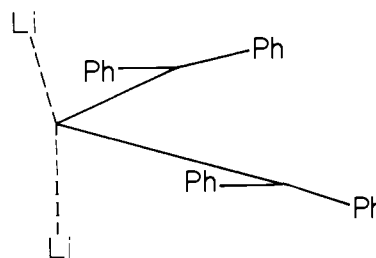


Figure 3. Postulated structure for Ph₂CCCPh₂, Li₂.

"dianion" 1-⁷Li₂: (i) a small (40.0 Hz) ¹³C-¹³C spin coupling constant ¹J(CC), in the range typical for sp³-sp² carbon-carbon bonds,⁴ is observed; (ii) chemical shifts for carbons C(1), C(2), and C(3) are shifted downfield [+72 ppm for C(2) and C(1) and +12 ppm C(3)] from the corresponding values for (4); (iii) at -82 °C, the C(2) resonance is not resolved in contrast to the resonances from C(1) and C(3); (iv) at -14 °C, the C(2) resonance is resolved into a triplet (*J* = 40.0 Hz).

In order to improve the resolution of the C-Li coupling at C(2), the analogous experiment was performed with 95% ⁶Li on 3-2-¹³C and 3-¹³C₃. In the first case, the C(2) resonance was a pentuplet down to -116 °C (see Figure 2), consistent with equivalent coupling of the carbon atom to two lithium atoms of spin 1, while the C(1) resonance in the second case showed no coupling >2 Hz at the same temperature. The magnitude of the coupling constants (*J* = 9 Hz), is reminiscent of that obtained for phenyllithium (*J* = 8), which exists in dimeric form in solution.^{7a} However, the ⁶Li NMR spectrum showed a doublet (*J* = 9 Hz),^{7b} with some asymmetry attributed to contamination by 4. The ⁶Li NMR spectrum derived from ¹³C-nonenriched 3 yielded a singlet at the same chemical shift. Thus we conclude that the title compound 1-Li₂ exists as a monomer and has C₂ symmetric structure in which there is a strong interaction between C(2) and equivalent lithium atoms (e.g., Figure 3).

Since ¹J(CC) for 1-Li₂ is well below the value expected for sp-sp² carbon-carbon bonds (40 vs. 103 Hz for the parent allene 3), we conclude that the C(1), C(2), C(3) framework of 1-Li₂ is bent. In the bent structure, the central carbon C(2) must bear an electron pair in an "sp²" orbital. In the structurally related bis(lithiobenzyl) ketone, each lithium bridges an oxygen atom, a terminal atom, and an ortho phenyl carbon.⁸ A similar structure

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(5) Tetraphenylallene-¹³C₃ (90% ¹³C enrichment at each allenic carbon) was synthesized starting from barium carbonate (90% ¹³C). Pure isolated intermediates were (yields in the brackets) (a) diphenylmethane-¹³C (64%; calculated on BaCO₃), (b) diphenylacetic-¹³C₂ (94%), and (c) diphenylacetic-¹³C₂ acid barium salt (66%) and tetraphenylallene-¹³C₃ (30%); actual yields were larger since in step c diphenylacetic-¹³C₂ acid and diphenylmethane-¹³C were recovered with high yields.

(6) 1,1,3,3-Tetraphenylpropene-¹³C₃ was prepared by lithium metal reduction in tetrahydrofuran at -78 °C of tetraphenylallene-¹³C₃ and quenching the resultant reaction mixture with methanol.

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for 1-Li₂ would satisfy both symmetry and bonding requirements, with the C(2)-Li coupling reflecting analogous bonding to that in phenyllithium.⁷ We note that Streitwieser's calculation^{2b} restricted the lithium atoms to the plane bisecting the molecule. This structure represents one limiting form of an ensemble in which we allow the Li-C-Li plane to rotate with respect to the C-C-C plane. The other limiting form, of course, is the planar tetracoordinate carbon predicted for certain dilithio carbon derivatives.⁹ Since all such forms minimally satisfy our C₂ symmetry requirements, we can only reemphasize the curious nature of bonding in organolithium compounds.

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Temperature-Independent Isotope Effects in Hydro Transfer. Do They Signify a Bent Transition State?¹

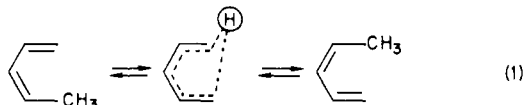
Duncan J. McLennan* and Peter M. W. Gill

Department of Chemistry
University of Auckland
Auckland, New Zealand
Received August 6, 1984

A number of remarkable temperature-independent primary kinetic isotope effects (KIE's) for reactions involving hydro transfer have recently been reported by Kwart and his co-workers.²⁻⁴ They have contended that reactions displaying this phenomenon pass through transition states (TS's) in which the D...H...A (D = donor, A = acceptor) angle is significantly less than 180°, whilst processes having a normal temperature dependence of k_H/k_D , with $[\Delta E_a]_D^H$ ranging up to about 1.2 kcal mol⁻¹, are characterized by linear TS's having angles close to 180°.

In particular, Kwart argued that the $[\Delta E_a]_D^H$ of 1.4 kcal mol⁻¹ attending the degenerate [1,5] sigmatropic H shift of *cis*-1,3-pentadiene⁵ afforded proof of linear TS geometry, whilst the $[\Delta E_a]_D^H \approx 0$ that he found for the same process in a cyclic system resulted from enforced nonlinear TS geometry.⁶

No theoretical reasons have been advanced to rationalize this dichotomy, and for this reason we commenced model calculations at the instigation of the late Harold Kwart. The particular system investigated was the above-mentioned sigmatropic rearrangement, eq 1, but other results indicate that the findings should be generally



- (1) Model Calculations of Isotope Effects. Part 10.
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(3) Kwart, H. *Acc. Chem. Res.* **1982**, *15*, 401-408.
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Table I. Primary KIE's and Their Temperature Dependence for the Sigmatropic Rearrangement of 1,3-Pentadiene^a

angle	k_H/k_D (0 °C) for model			
	A	B	C	D
180°	9.30 (1.20)	8.38 (1.12)	4.99 (0.82)	5.72 (0.90)
150°	7.23 (1.05)	7.12 (1.04)	4.07 (0.70)	4.63 (0.68)
120°	3.84 (0.69)	3.79 (0.70)	2.30 (0.39)	2.43 (0.43)
90°	1.97 (0.34)	1.68 (0.30)	1.21 (0.05)	1.05 (0.006)

^a $n_1 = n_2 = 0.50$ in all cases. Values of $[\Delta E_a]_D^H$ in parentheses (kcal mol⁻¹).

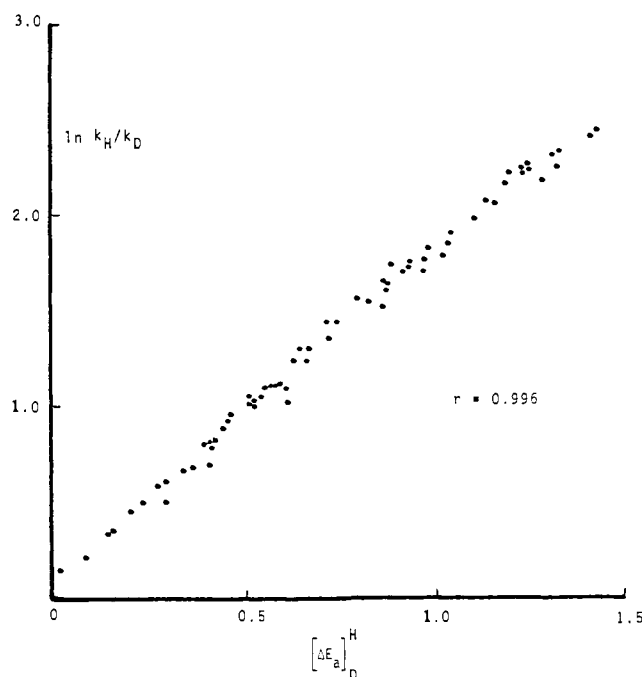
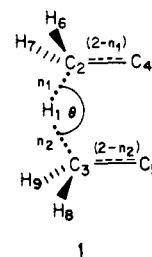


Figure 1. Relationship between the magnitude of k_H/k_D (0 °C) and the temperature dependence as expressed by $[\Delta E_a]_D^H$.

and widely applicable. To avoid complications associated with cyclic TS models, we adopted the cutoff model 1, and on the basis of various assumed geometries, we assigned force constants to coordinates which included the partial bonds by using conventional empirical formulations involving the bond orders n_1 and n_2 .⁷



Parameters varied were n_1 , n_2 , and θ , whilst many combinations of empirical formulations for the C₂...H...C₃ bending force constant and for the interaction force constants generating reaction coordinate motion were employed. Single temperature KIE's at fixed θ ($90 \leq \theta \leq 180^\circ$) displayed a dependence on n_1 and n_2 similar to that described for an earlier, simpler model.⁸ In Table I is displayed the model dependence of k_H/k_D for some cases where $n_1 = n_2 = 0.5$. Models A and B involve the generation of reaction coordinate motion by simple coupling of the C₂...H and H...C₃ stretching modes, model C includes heavy atom motion (an E2-like reaction coordinate⁹), and model D adds to this coupling of bending

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