of a sample of ethyl haematommate prepared by the method of St. Pfau.

Acknowledgments. The authors are grateful to Dr. Jon Clardy of Iowa State University and to the Committee for Research and Curriculum Development at the University of Northern Iowa for partial support for this work.

Registry No.—**1a**, 479-25-4; **1b**, 2524-37-0; **2**, 21855-43-6; **3**, 6780-49-0; **4**, 62392-80-7; **5**, 62392-81-8; **6**, 62392-82-9; *N*-bromosuccinimide, 128-08-5.

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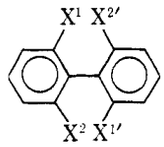
Steric Effects. 8. Racemization of Chiral Biphenyls

Marvin Charton

School of Science, Pratt Institute, Brooklyn, New York 11205

Received November 19, 1975

Adams[1] has suggested as a method of predicting the resolvability of chiral biphenyls that when the sum of certain group radii of the groups X^1 and X^2 in I is considerably greater than



I

2.90 Å, the biphenyl will be resolvable; when the sum is considerably less than 2.90 Å, the biphenyl will not be resolvable. We have examined the relationship between the υ steric parameters[2,3] and the Adams group radii. The υ parameters are a function of the van der Waals radii. They are defined by the relationship

$$\upsilon_X = r_{VX} - r_{VH} = r_{VX} - 1.20 \quad (1)$$

where r_{VX} and r_{VH} are the van der Waals radii of the X and H group, respectively. Values of υ were taken from our previous work.[2,3] The group radii used are given in Table I. Correlation was carried out with the equation

$$r_{GX} = m\upsilon_X + c \quad (2)$$

where r_{GX} is the group radius of the X group. Results of the correlation are reported in Table II. The results (set 1) are significant at the 99.9% confidence level (CL). Exclusion of the values for CO_2H and NO_2 (set 1A) results in very much improved correlation as is shown by the value of the F test for significance of the results. Thus, eq 2 has been verified. The deviation of CO_2H and NO_2 is not surprising as the υ values of these groups will be strongly dependent on the transition state of the reaction being studied.

New values of υ were calculated for the NO_2 and CO_2H groups from the appropriate r_{GX} values using set 1A of Table II. They are 0.59 and 0.37, respectively. The value for NO_2 seems reasonable, but the value for CO_2H appears to be too low.

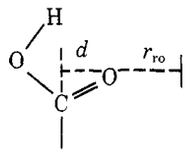
Table I. Data Used in Correlations[a]

1. Adams group radii
H, 0.94; F, 1.39; OH, 1.45; CO_2H, 1.56; NH_2, 1.56; Me, 1.73; Cl, 1.89; NO_2, 1.92, Br, 2.11; I, 2.20
2. Half-lives of 3′-substituted 2-NO_2-6CO_2H-2′-MeO-biphenyls in EtOH at 25 °C
H, 9.4; MeO, 98.1; Me, 332; C, 711; Br, 827; NO_2, 1905
3. Half-lives of 4′-substituted 2-NO_2-6-CO_2H-2′-MeO-biphenyls in MeAc at 25 °C
MeO, 2.6; Me, 3.6; Cl, 12; Br, 25; NO_2, 115
4. Half-lives of 5′-substituted 2-NO_2-CO_2H-2′-MeO-biphenyls in EtOH at 25 °C
H, 9.4; OMe, 10.8; Me, 11.5; Cl, 31; Br, 32; NO_2, 35.4

[a] All data from ref 1 and 6.

These conclusions are based on the point that a planar π-bonded substituent can exist in two extreme conformations with respect to a benzene ring, coplanar or perpendicular. In the perpendicular case, the half-thickness of the substituent determined its υ value, which is minimal and will be referred to as υ_{min}. In the coplanar case the υ value can be calculated as shown in Chart I. It represents a maximal value of υ and is

Chart I



designated υ_{max}. Thus,

$$\upsilon_{max} = d + r_{VO} - 1.20 \quad (3)$$

where r_{VO} is the van der Waals radius of oxygen. Values of υ_{max} and υ_{min} for NO_2 and CO_2H are 1.30, 0.35, and 1.48, 0.50, respectively.

Our results make possible the calculation of Adams group radii from the large number of υ values available, and therefore permit the estimation of optical stability in biphenyls of type I for a wide range of substituents.

We now turn our attention to rates of racemization of substituted biphenyls. Adams and co-workers[1] have measured half-lives for the racemization of 2-NO_2-6-CO_2H-2′-MeO-biphenyls substituted in either the 3′, the 4′, or the 5′ position. These data are reported in Table I. The half-life is related to the rate constants for racemization. The effect of the substituent in the 3′ position has been ascribed to the "buttressing effect". According to Eliel[4] and Ferguson[5] the effect of the substituents in the 4′ position is not well understood. The effect of substituents in the 5′ position is also said to be due to buttressing.[4,5] To investigate these various effects we have examined the correlation of the half-lives by means of the equation

$$\log t_{1/2,X} = \alpha\sigma_{IX} + \beta\sigma_{RX} + \psi\upsilon_X + h \quad (4)$$

in which the σ_I constants[6] and the σ_R constants[6] are measures of the localized (field and/or inductive) and delocalized (resonance) electrical effects. The results of the correlations with eq 4 are given in Table III. The σ_I constants are from our previous work,[6] the σ_R constants were obtained from

$$\sigma_R = \sigma_p - \sigma_I \quad (5)$$

The necessary σ_p constants are from the compilation of McDaniel and Brown.[8] The υ values, as before, are from our collection[2] with the exception of the NO_2 group, for which the

Table II. Results of Correlations with Equations 2 and 9

Set	Slope	Intercept	r^a	F^b	$s_{est}{}^c$	$s_{slope}{}^c$	$s_{intercept}{}^c$	n^d
1	1.56	1.00	0.913	39.97[e]	0.163	0.247[e]	0.118[e]	10
1A	1.67	0.940	0.992	394.3[e]	0.0547	0.0841[e]	0.0410[e]	8
4B	0.859	1.01	0.906	18.23[f]	0.129	0.201[g]	0.0801[e]	6

[a] Correlation coefficient. [b] F test for significance of correlation. [c] Standard errors of the estimate, slope, and intercept. [d] Number of points in set. [e] 99.9% confidence level (CL). [f] 97.5% CL. [g] 98.0% CL.

Table III. Results of Correlations with Equations 5, 7, and 8

Set	α	β	ψ	h	R^a	F^b	$r_{12}{}^c$	$r_{13}{}^c$
2	0.630	0.360	2.87	1.03	0.992	40.07[f]	0.104	0.626
2A	0.684		2.83	0.978	0.987	58.67[j]		0.626
3	1.55	1.27	0.761	0.398	0.990	15.76[m]	0.374	0.432
3A	1.61	1.55		0.831	0.985	32.59[i]	0.374	
4	0.615	0.226	0.429	0.934	0.964	8.646[m]	0.104	0.626
4A	0.648		0.399	0.899	0.947	13.04[i]		0.626

Set	$r_{23}{}^c$	$s_{est}{}^d$	$s_\alpha{}^d$	$s_\beta{}^d$	$s_\psi{}^d$	$s_h{}^d$	n^e
2	0.025	0.168	0.341[g]	0.352[g]	0.401[h]	0.162[i]	6
2A		0.170	0.339[k]		0.402[l]	0.154[l]	6
3	0.725	0.192	0.388[k]	0.624[g]	1.15[n]	0.687[n]	5
3A		0.163	0.319[i]	0.391[o]		0.177[i]	5
4	0.025	0.155	0.233[k]	0.241[g]	0.274[g]	0.111[h]	6
4A		0.113	0.226[o]		0.267[g]	0.102[l]	6

[a] Multiple correlation coefficient. [b] F test for significance of correlation. Superscripts indicate CL. [c] Partial correlation coefficients of σ_I on σ_R, σ_I on υ, σ_R on υ. Confidence level <90.0% unless otherwise indicated by superscripts. [d] Standard errors of the estimate, α, β, ψ, and h. Superscripts indicate CL of Student's t test. [e] Number of points in set. [f] 97.5% CL. [g] 50.0% CL. [h] 98.0% CL. [i] 95.0% CL. [j] 99.5% CL. [k] 80.0% CL. [l] 99.0% CL. [m] <90.0% CL. [n] 20.0% CL. [o] 90.0% CL.

value of 0.59, calculated above, was used. The half-lives of the 3′-substituted 2-NO_2-6-CO_2H-2′-MeO-biphenyls show a good correlation with eq 4 (set 2). The Student's t tests show that α and β are not significant while ψ is significant. The value of β is small as is expected for a substituent in the meta position. Correlation was therefore examined with the equation

$$\log t_{1/2,X} = \alpha\sigma_{IX} + \psi\upsilon_X + h \quad (6)$$

The result was an excellent correlation (set 2A). Although α still was not significant, it was more meaningful than it had been in the correlation with eq 5. It is quite possible that had there been more points in the set, α would have been significant. The ψ value is highly significant. Furthermore, the magnitude of ψ is considerably greater than that of α. This is in accord with a buttressing effect of the 3′ substituent as the predominant factor in its behavior. There may also be an electrical effect of the 3′ substituent upon the electron density in the C^1–C^1 bond which affects the ease of rotation.

The half-lives of the 4′-substituted compounds show no significant correlation with eq 5, undoubtedly due to the small size of the set, which contains only five points (set 3). As the Student's t test showed the least significance for ψ, correlation was carried out with the equation

$$\log t_{1.2,X} = \alpha\sigma_{IX} + \beta\sigma_{RX} + h \quad (7)$$

giving fair results (set 3A). Both α and β were significant as determined by the Student's t test. Undoubtedly, better results would have been obtained had more data been available. We interpret the successful correlation with eq 7 to mean that the 4′ substituent exerts an electrical effect upon the C^1–$C^{1'}$ bond which affects the ease of rotation, and does not produce any steric effect whatsoever. This result is in agreement with the reports by a number of authors of correlations of energy barriers to internal rotation with the Hammett equation.[9] Thus, the hitherto obscure effect of the 4′ substituents can now be well understood.

The half-lives of the 5′-substituted compounds show no significant correlation with eq 4 (set 4). Again, the value of β is small. The Student's t test shows that ψ is more significant than β. Therefore, correlation was carried out with eq 7. The result was a fair correlation, with α being significant and ψ not significant (set 4A). Correlation was then carried out with the equation

$$\log t_{1/2X} = \alpha\sigma_{IX} + h \quad (9)$$

Results of this correlation are given in Table II (set 4B). A good result was obtained. Thus, 5′ substituents appear to exert only an electrical effect upon the rate of racemization. The difference between the 3′ and 5′ substituents is that the former are adjacent to a MeO group whereas the latter are adjacent to a very much smaller hydrogen atom and therefore do not show a buttressing effect.

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