then extracted with three 50-ml portions of ether. The solvent was stripped from the dried ether (potassium carbonate) and the residue was distilled to give 14.3 g (89%) of pure 1,1-diphenylhydrazine, bp 120° (1.1 mm). Its hydrazone with *p*-nitrobenzaldehyde melted at 131–132° (lit.[6] mp 131°).

A solution of 10.2 g (0.036 mol) of *t*-butyl 3,3-diphenylcarbazate in 100 ml of methanol containing 5 ml of concentrated hydrochloric acid was heated under reflux for 3 hr. Work-up as above gave 7.7 g (98%) of 1,1-diphenylhydrazine hydrochloride, mp 165–170°. Attempted hydrolysis of this ester under strongly alkaline conditions was ineffective. Ethyl 3,3-diphenylcarbazate was formed in 97% yield after 15 days of reflux of a solution of 15 g of diphenylcarbamyl azide. (Reference 4 does not give the amounts used when 30 days were required to complete the reaction.)

***t*-Butyl 3,3-Diphenylcarbazate.**—A solution of 22.1 g (0.09 mol) of diphenylcarbamyl azide, mp 65°, in 150 ml of *t*-butyl alcohol and 50 ml of toluene was heated under reflux for 5 days. Removal of the solvent left 25 g (92%) of *t*-butyl 3,3-diphenylcarbazate. One recrystallization from cyclohexane gave 20.4 g (76%) of product, mp 122.5–124°.

Anal. Calcd for $C_{17}H_{20}N_2O_2$: C, 71.83; H, 7.04; N, 9.87. Found: C, 71.57; H, 7.54; N, 9.93.

Biphenylenecarbamyl Azide.—The procedure used for the preparation of diphenylcarbamyl azide gave 39 g (98%) of biphenylenecarbamyl azide, mp 92–93°, from 39 g of carbamyl chloride.

Anal. Calcd for $C_{13}H_8N_4O$: C, 66.09; H, 3.41; N, 23.72. Found: C, 65.91; H, 3.57; N, 22.92.

***t*-Butyl 3,3-Biphenylenylcarbazate.**—A solution of 39.0 g (0.16 mol) of biphenylenecarbamyl azide in 200 ml of *t*-butyl alcohol and 50 ml of toluene was heated under reflux for 10 days. Upon cooling, 4.5 g of white silky solid precipitated, mp >300°. This is probably bis(biphenylenyl)carbohydrazide. Removal of the solvent left 38 g (82%) of the ester, mp 120–122°.

Anal. Calcd for $C_{17}H_{18}N_2O_2$: C, 72.31; H, 6.42; N, 9.92. Found: C, 72.86; H, 6.38; N, 9.80.

N-Aminocarbazole Hydrochloride.—A solution of 38.0 g (0.13 mol) of *t*-butyl 3,3-biphenylenylcarbazate in 200 ml of methanol containing 18 ml of concentrated hydrochloric acid was heated under reflux for 5 hr. Removal of the solvent left a white solid which was washed with 100 ml of ether. N-Aminocarbazole hydrochloride was obtained (28.5 g, 97%) as silky white crystals, mp 155–156° (dec).

N-Aminocarbazole.—A suspension of 28.5 g (0.13 mol) of N-aminocarbazole hydrochloride in 200 ml of water was made strongly alkaline by the addition of 10 g of sodium hydroxide. The solution was then extracted with two 200-ml portions of ether. Evaporation of the dried ether extract (potassium carbonate) and recrystallization of the residue from ethanol gave 22.7 g (96%) of pale tan needles, mp 147–148°. Its N-benzoyl derivative melted at 230–231° (lit.[7] mp 231–232°).

Registry No.—II, Ar = Ph, 17223-83-5; III, Ar = Ph; R = *t*-Bu, 17223-84-6; IV, Ar = Ph, 530-50-7; IV, Ar = Ph·HCl, 530-47-2; biphenylenecarbamyl azide, 17255-74-2; *t*-butyl 3,3-biphenylenylcarbazate, 17223-87-9; N-aminocarbazole hydrochloride, 17223-86-8; N-aminocarbazole, 17223-85-7.

[6] H. Labhardt and K. Zembrzuski, *Ber.*, **32**, 3062 (1899).

[7] P. A. S. Smith and H. G. Pars, *J. Org. Chem.*, **24**, 1325 (1959).

Bond Deformations in Conjugated Molecules

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Frequent attempts have been made to evaluate the geometries of conjugated molecules *via* utilization of bond-order–bond-length relationships.[1] In a recent examination, the possible inadequacy of this approach was noted for the nonalternant molecule, fluoranthene.[2] For this system, consideration of the underlying σ network leads to a significantly different calculated structure.

The effects of such σ strain on the π energies of cyclic conjugated systems have been considered by Gleicher[3] and by Allinger and his coworkers.[4,5] In these studies attention was particularly focused on possible deviations from planarity of certain nonalternant molecules.

Discrepancies have been noted between experimentally obtained bond lengths and those calculated from bond orders for alternant hydrocarbons. It would be attractive to explain these differences as due to a similar relief of strain-producing factors. In these systems angle strain represents a near-negligible factor. The chief driving force toward possible bond deformation would be to reduce the strain associated with severe nonbonded interactions. To test this, a series of polycyclic systems related to phenanthrene was chosen for study. Bond deformations have been considered as energetically ineffective means of relieving molecular strain.[6] The relatively small changes in bond length treated here, however, do lead to an observable decrease in strain. All of the molecules studied were assumed to be planar. The complexity of including out-of-plane motions was felt to be prohibitive even though such calculations have previously appeared.[7]

The following approach was utilized. A trial structure was constructed from bond lengths based on SCF-MO bond orders.[8] A minimum strain energy was then found by systematically varying the coordinates of the atoms.[9,10] As in earlier work from this laboratory, the in-plane bending force constants and carbon–hydrogen stretching force constant were obtained from Cyvin's analysis of benzene[11] and the nonbonded interaction potentials from Bartell's study on intramolecular van der Waals forces.[12] The carbon–carbon stretching force constants were assumed to be a function of the bond length.[2] These were correlated by the relationship developed by Dewar and Schmeising.[13] Although attention is principally directed to long, easily deformable bonds, such as e–f in phenanthrene, Table I contains the values of all calculated and experimental bond lengths. The structures used appear in Chart I.

The unfavorable nonbonded interactions are least serious in phenanthrene. Minimization of the strain energy leads to a structure which differs only slightly from the starting geometry. Two bonds, a–i and h–i, the experimental values of which are unexpected, are not changed in this treatment.[14] It has been suggested

[1] L. Salem, "Molecular Orbital Theory of Conjugated Systems," W. A Benjamin, Inc., New York, N. Y., 1966, pp 134–148.

[2] G. J. Gleicher, *J. Amer. Chem. Soc.*, **90**, 3397 (1968).

[3] G. J. Gleicher, *Tetrahedron*, **23**, 4257 (1967).

[4] N. L. Allinger, *ibid.*, **22**, 1367 (1966).

[5] N. L. Allinger, M. A. Miller, L. W. Chow, R. A. Ford, and J. C. Graham, *J. Amer. Chem. Soc.*, **87**, 3430 (1965).

[6] G. Ferguson and J. M. Robertson, *Advan. Phys. Org. Chem.*, **1**, 203 (1963).

[7] C. A. Coulson and C. W. Haigh, *Tetrahedron*, **19**, 527 (1963), and references cited therein.

[8] M. J. S. Dewar and G. J. Gleicher, *J. Chem. Phys.*, **44**, 759 (1966).

[9] K. B. Wiberg, *J. Amer. Chem. Soc.*, **87**, 1070 (1965).

[10] G. J. Gleicher and P. von R. Schleyer, *ibid.*, **89**, 582 (1967).

[11] S. Cyvin, *Acta Chem. Scand.*, **11**, 1499 (1957).

[12] L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960).

[13] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **11**, 96 (1960).

[14] J. Trotter, *Acta Cryst.*, **16**, 605 (1963).

TABLE I

BOND LENGTHS[a]

Molecule	Bond[b]	Calculated length: From bond orders	Calculated length: After minimization	Experimental values
Phenanthrene (I)	a–b	1.384	1.384	1.381
	b–c	1.412	1.412	1.398
	c–d	1.385	1.383	1.383
	d–e	1.415	1.415	1.405
	e–f	1.449	1.455	1.448
	g–h	1.363	1.370	1.372
	h–i	1.445	1.450	1.390
	a–i	1.417	1.417	1.457
	e–i	1.403	1.403	1.404
Chrysene (II)	a–b	1.381	1.381	1.360
	b–c	1.416	1.415	1.392
	c–d	1.381	1.377	1.379
	d–e	1.420	1.420	1.405
	e–f	1.442	1.456	1.468
	f–g	1.398	1.399	1.397
	g–h	1.436	1.437	1.423
	h–i	1.368	1.368	1.365
	i–j	1.439	1.440	1.418
	a–j	1.420	1.422	1.427
	e–j	1.405	1.405	1.406
Triphenylene (III)	a–b	1.391	1.389	1.377
	b–c	1.406	1.406	1.402
	a–e	1.409	1.412	1.416
	e–d	1.404	1.404	1.415
	e–f	1.458	1.474	1.447
Perylene (IV)	a–b	1.378	1.380	1.370
	b–c	1.419	1.417	1.418
	c–d	1.383	1.392	1.397
	d–f	1.429	1.433	1.425
	f–g	1.409	1.411	1.424
	a–g	1.427	1.425	1.411
	d–e	1.465	1.496	1.471

[a] In ångström units. [b] Lettering is shown in Chart I.

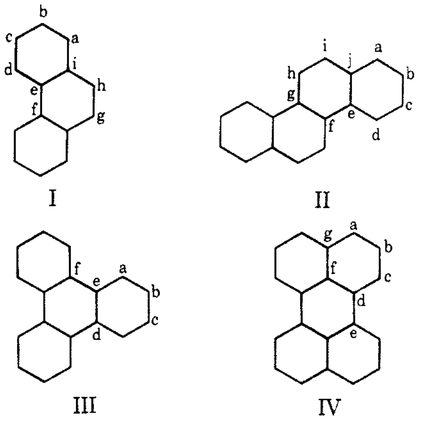
that these lengths are probably not caused by intramolecular factors.[6] In chrysene the total unfavorable hydrogen–hydrogen interactions should be twice those of phenanthrene. It is gratifying to note that after minimization the long bond, e–f is in much better agreement with the experimental value.[15]

Triphenylene and perylene should be capable of a much greater amount of bond deformation. The nonbonded interactions can be lessened by stretching long carbon–carbon bonds with relatively weak force constants. A modern structure determination has been performed on triphenylene.[16] Bond e–f appears very much shorter than calculated. This is disconcerting, as one would presume little aromatic character to be associated with the central ring of this system. The calculated π-bonding energy of triphenylene is only 4.4% in excess of that of three benzene units. Extensive delocalization in the central ring could only be achieved if the outer rings assumed much less stable quinoid structures.

Reliable X-ray data also exist for perylene.[17] The "long bond" here is also shorter than that calculated. The π-bonding energy of this molecule is only 2.5% in excess of two naphthalene units. No uncharged resonance forms can be drawn in which bond d–e has double-bond character. Earlier, less precise data showed a value for this bond of 1.50 Å.[18] The *peri* bonds in the related molecule, quaterylene, have an average value of 1.527 Å.[19] Based on this, the corresponding value for perylene appears too short. The formalism of Dewar and Schmeising[20] leads to the expectation of a minimal length for this bond of 1.48 Å which might be further elongated by nonbonded interactions. A recent substantiation of the Dewar and Schmeising formalism has been obtained for bis alicyclic molecules.[21]

CHART I

SYSTEMS RELATED TO PHENANTHRENE



Certain less complex systems have also been examined. In (18)-annulene the lengths of the six "outer" bonds are 1.420 Å while the twelve "inner" bonds have values of 1.382 Å.[22] Murrell and Hinchliffe have calculated this to be due to changes in the sigma system.[23] The values for these bonds obtained from the bond orders are 1.404 and 1.400 Å, respectively. After minimization they were 1.426 and 1.404 Å in partial agreement with experiment. Unlike the polycyclic systems, there is appreciable deformation of the bond angles from their equilibrium value.

The most elementary system this treatment could be applied to is 1,3-butadiene. As might be expected the calculated bond lengths are not appreciably modified by minimization. The values are 1.345 Å for the terminal bonds and 1.470 Å for the central bond. These compare very favorably with the experimental values of 1.343 and 1.467 Å.[24] 2,3-Dimethyl-1,3-butadiene shows the corresponding minimized values of 1.345 and 1.490 Å. The experimental values are 1.349 and 1.504 Å.[25] The calculations here have been particularly effective in accounting for the increase in the central bond length due to probable methyl–hydrogen interactions.

It would appear that inclusion of strain factors in conjugated molecules may lead to improvements in

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(15) D. M. Burns and J. Iball, *Proc. Roy. Soc.* (London), **A257**, 491 (1960).

(16) F. R. Ahmed and J. Trotter, *Acta Cryst.*, **16**, 503 (1963).

(17) A. Camerman and J. Trotter, *Proc. Roy. Soc.* (London), **A279**, 129 (1964).

(18) D. M. Donaldson, J. M. Robertson, and J. G. White, *ibid.*, **A220**, 311 (1953).

(19) H. N. Shrivastava and J. C. Speakman, *ibid.*, **A257**, 477 (1960).

(20) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959).

(21) R. A. Alden, J. Kraut, and T. G. Traylor, *J. Amer. Chem. Soc.*, **90**, 74 (1968).

(22) J. Bregman, F. L. Hirshfeld, D. Rabinovich, and G. M. J. Schmidt, *Acta Cryst.*, **19**, 227 (1965).

(23) J. N. Murrell and A. Hinchliffe, *Trans. Faraday Soc.*, **62**, 2011 (1966).

(24) W. Haugen and M. Traetteberg, *Acta Chem. Scand.*, **20**, 1726 (1966).

(25) C. F. Aten, L. Hedberg, and K. Hedberg, *J. Amer. Chem. Soc.*, **90**, 2463 (1968).

calculated geometries. Although the results presented here are not in uniform agreement with experiment, it is felt that some encouragement may be taken from them. It also is of interest to note, in the cases of triphenylene and perylene, that the calculated lengths of the long bonds are in accord with present theory.

Registry No.—I, 85-01-8; II, 218-01-9; III, 217-59-4; IV, 198-55-0.

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Correlation of the Chirality of the Disulfide Group with Its Molecular Ellipticity

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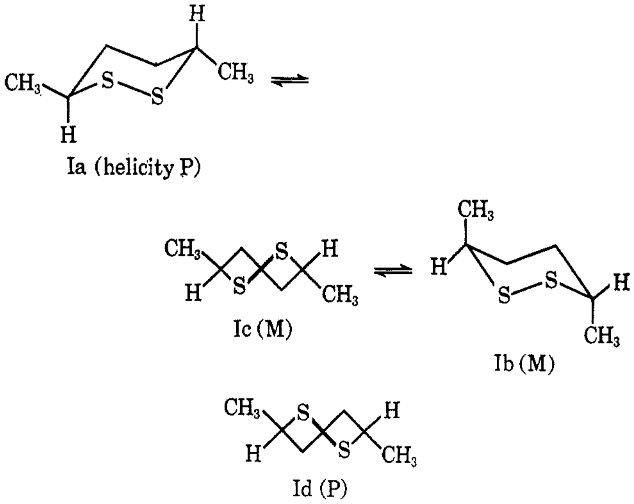
In molecules possessing a C–S–S–C group in the vicinity of one or more asymmetric centers, an unequal distribution of the M and P[1] chiral C–S–S–C groups (left-handed helix, M, and right-handed helix, P) may be maintained. It has been shown that the electronic transitions associated with this chiral C–S–S–C group are optically active.[2] The ORD and CD spectra of gliotoxin,[3] a compound possessing a C–S–S–C group of known absolute configuration (chirality M), have been studied. In gliotoxin the negative CD peak at 340 mμ was associated with the left-handed (M) chirality of the disulfide group. However, the authors were not certain whether the sign of the CD peak was dominated by the skew sense of the disulfide. That this is the case was shown very recently by Carmack and Neubert.[4] Here, we confirm and extend these previous observations and provide further evidence for the predominantly chair conformation of 1,2-dithianes.

2,5-Hexanediol was separated into the *meso* and *dl* isomers by crystallization of the bis(hydrogen phthalate) esters. The higher melting bis(hydrogen phthalate) was partially resolved by crystallization of the dibrucine salt. The 2,5-hexanediol, obtained from the dibrucine salt, was chromatographed on alumina. Its rotation, $[\alpha]^{29}\mathrm{D}$ −17.6° (ethanol), indicated that it was predominantly (2*R*,5*R*)-2,5-hexanediol.[5] The optically active diol was converted into the di-*p*-toluenesulfonate which, in turn, was converted with sodium disulfide into the desired *trans*-3,6-dimethyl-1,2-dithiane[6] (I). This compound was separated from an accompanying 12% *cis*-3,6-dimethyl-1,2-dithiane by preparative vapor phase chromatography. If one assumes that the displacement reaction went with 100% inversion of configuration and that the *cis*-3,6-dimethyldithiane resulted from a small quantity of the *meso*-2,5-hexanediol still present, then the (3*S*,6*S*)-(+)-*trans*-3,6-dimethyl-1,2-dithiane (IaP) so obtained should be 85% optically pure.

(2*S*,5*S*)-2,5-Hexanediol, $[\alpha]^{29}\mathrm{D}$ +14.0° (ethanol), was obtained by hydrolysis of the mother liquors from the above resolution. This diol was converted into the di-*p*-toluenesulfonate which was crystallized to constant melting point and constant rotation. Reaction of this di-*p*-toluenesulfonate, which we believe to be optically pure, with sodium disulfide yielded (3*R*,6*R*)-(−)-*trans*-3,6-dimethyl-1,2-dithiane (IaM), $[\alpha]^{28}\mathrm{D}$ −276° (ethanol). Comparison of the rotation of this (3*R*,6*R*) enantiomer with that of the optically impure (3*S*,6*S*) enantiomer indicates that the (3*S*,6*S*)-(+)-*trans*-3,6-dimethyl-1,2-dithiane (IaP) was 84% optically pure. This agrees within experimental error with the optical purity calculated from the rotation of the (2*R*, 5*R*)-2,5-hexanediol. Vapor phase chromatography of the (−)-3,6-dimethyl-1,2-dithiane showed none of the *meso* isomer. This provides good evidence that our initial assumption of 100% inversion of configuration in the displacement reaction is probably correct.


Ia (helicity P)

Ic (M)

Ib (M)

Id (P)

The corresponding *cis*-3,6-dimethyl-1,2-dithiane (II) was synthesized from the *meso*-2,5-hexanediol and was purified by chromatography on a silica gel column. Purity was confirmed by gas chromatography.

Kalff and Havinga[7] have shown that the dipole moment of 1,2-dithiane is in agreement with that calculated for the chair conformation for the compound. The nmr spectra[8] of 1,2-dithiane and substituted 1,2-dithianes provide good evidence for the chair conformation of these compounds. An X-ray analysis of the structure of *trans*-1,2-dithiane-3,6-dicarboxylic acid has shown that the dithiane ring has the chair conformation with the substituents in equatorial positions.[9] To provide further evidence for the chair conformation of

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(1) R. S. Cahn, C. Ingold, and V. Prelog, *Angew. Chem. Intern. Ed. Engl.*, **5**, 385 (1966).

(2) A. Fredga, *Acta Chem. Scand.*, **4**, 1307 (1950); C. Djerassi, H. Wolf, and E. Bunnenberg, *J. Amer. Chem. Soc.*, **84**, 4552 (1962).

(3) A. F. Beecham, J. Fridrichsons, and A. Mc L. Mathieson, *Tetrahedron Lett.*, 3131 (1966); A. F. Beecham and A. Mc L. Mathieson, *ibid.*, 3139 (1966).

(4) M. Carmack and L. A. Neubert, *J. Amer. Chem. Soc.*, **89**, 7134 (1967). The work reported here was practically completed when the communication from Dr. Carmack appeared.

(5) K. Serck-Hanssen, S. Ställberg-Stenhagen, and E. Stenhagen, *Ark. Kemi*, **5**, 203 (1953).

(6) N. Isenberg and H. F. Herbrandson, *Tetrahedron*, 1067 (1965).

(7) H. T. Kalff and E. Havinga, *Rec. Trav. Chim. Pays-Bas*, **81**, 282 (1962).

(8) G. Claeson, G. Androes, and M. Calvin, *J. Amer. Chem. Soc.*, **83**, 4357 (1961); A. Luettringhaus, S. Kabuss, W. Maier, and H. Freiburg, *Z. Naturforsch.*, **16B**, 761 (1961).

(9) O. Foss and L. Schotte, *Acta Chem. Scand.*, **11**, 1424 (1957); O. Foss and T. Reistad, *ibid.*, 1427 (1957).