Tetrahedron Vol. 41, No. 1, pp. 121 to 128, 1985
Printed in Great Britain.

0040-4020/85 $3.00 + .00

LINKAGE KINEMATICS AND CONFORMATIONAL ANALYSIS

J EDDIE BAKER

Department of Applied Mechanics, The University of New South Wales
P.O. Box 1, Kensington, N.S.W. 2033, Australia

(*Received in UK* 20 *August* 1984)

Abstract - Spatial linkage kinematics and chemical conformational analysis began to be established at about the same time and have experienced somewhat similar histories, without any direct contact between them. It has recently become clear that the two areas of study are strongly related in places, and that interdisciplinary research should be of mutual benefit. This paper is intended to demonstrate the ways in which the techniques of linkage kinematics can provide insights and analytical tools for investigating flexible states of cyclic molecules. It is, necessarily, exploratory and descriptive in some measure, but there is also presented a worked example, in order to illustrate the applicability of kinematic geometry in resolving an apparent paradox of conformational analysis.

INTRODUCTION

The correspondence between a special linkage of Bricard[1] and the flexible form of the cyclohexane molecule was noted independently by chemists (Dunitz and Waser[2]) and a kinematically-inclined mathematician (Bottema[3]). Recently it has been shown (Baker[4]) that there may be a direct theoretical connection between the minimum energy conformations of cyclohexane's flexible state and the stationary configurations of the corresponding Bricard linkage. The purpose of this article is to demonstrate that the methods of spatial linkage kinematics are of value in seeking flexible forms of cyclic molecules and in explaining seeming paradoxes among conformational isomers.

Conformational analysis is a structurally-based discipline. Although one is able to distinguish between some conformational isomers on a purely geometrical basis, and one is able to calculate the potential energy of any particular configuration without recourse to kinetics, the very nature of a flexible form demands a consideration of changing geometry for a complete understanding of the mechanism. The symmetries put to use by workers in this field of organic chemistry are of value, but they can also be quite misleading, if one is tempted to make inferences about flexible forms of one molecule as a consequence of what was observed for another.

The work of Dunitz and Waser[2] is quoted often in the chemical literature as a principal reference, both for the means of detecting flexible forms of molecules and for general guidance in the mathematical modelling of molecules. There is no doubt that the authors put forward a cogent and creditable account of parametric conditions which separate mobile spatial hexagons from rigid ones, but within rather narrow confines. They adopt a static technique, based on freedom and constraint and the simplifying characteristics of various symmetries. It has already been pointed out that motion geometry is a more appropriate medium. Rather than employing a synthetic line geometry, however, we use here the more searching analytical tool of screw system algebra. We shall not, consequently, be restricted to special configurations, and we shall be in a position to draw upon a considerable bank of prior results.

There is a clear relationship, indeed a continuum, between an architectural or chemical structure and a mechanical linkage. In fact, a molecular ring, with the admission of flexible states, is able to exhibit the whole gamut of forms, from rigidity, through instantaneous mobility, to full-cycle mobility. One has only to determine which portions of the ring constitute rigid bodies and which function as joints. Such considerations are readily attended to (Baker[4-7]). (The reader who wishes to peruse ref. 6 is advised that some unwarranted editorial amendments were made to this article, altering its intent in places, and so the author should be contacted for details of the offending sections.) Although not treated here specifically, it should also be mentioned that there is another technique in linkage kinematics which is directly applicable to engineering and architectural structures and to chemical molecules, namely, that of mechanical network analysis. This topic has now reached a high degree of sophistication and effectiveness (Davies[8-11]), and is quite capable of analysing a chain, loop or spheroid of organic molecules of given configuration.

THE MOTION SCREW AND MOBILITY

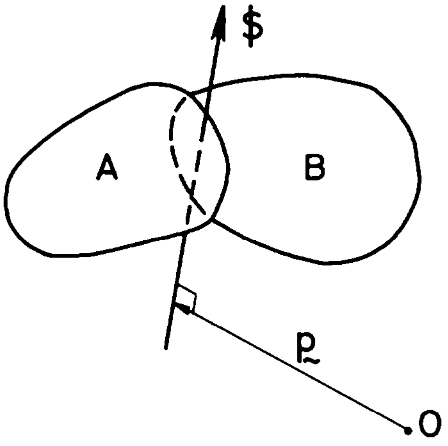

Fig. 1

In Fig. 1, A and B are two essentially rigid bodies (such as pistons, treadles or carbon atoms), and $\$$ is an axis of relative rotation between them (such as a hinge, an axle or a single covalent bond). Having designated the origin O of some fundamental frame of reference, $\underset{\sim}{p}$ being the normal vector from O to $\$$, we define the screw motor

$$\underset{\sim}{S} = (\underset{\sim}{\omega},\underset{\sim}{\mu}) \;,$$

a 6-element vector, made up as follows.

$\underset{\sim}{\omega}$ is the angular velocity vector of $\$$, incorporating a spatial orientation and a magnitude ω of relative angular speed.

$\underset{\sim}{\mu}$ is the (linear) velocity relative to A of a point in B instantaneously located at O, so that

$$\underset{\sim}{\mu} = \underset{\sim}{p} \times \underset{\sim}{\omega} \;.$$

It is sometimes convenient to utilise the instantaneous screw axis (ISA) vector

$$\underset{\sim}{\$} = (\hat{\underset{\sim}{\omega}},\hat{\underset{\sim}{\mu}}),$$

where

$$\hat{\underset{\sim}{\omega}} = \frac{\underset{\sim}{\omega}}{\omega} \qquad \hat{\underset{\sim}{\mu}} = \frac{\underset{\sim}{\mu}}{\omega}.$$

In the restricted form presented here, the ISA vector is identical to the entity known as the unit line vector, and is directly related to Plücker co-ordinates.

The screw motor is a basic element in analysing the degree of mobility of a (mechanical) linkage, which may be defined as an assemblage of jointed rigid bodies with the prime characteristic of gross relative motion between them. In Fig. 2, a linkage is illustrated schematically in its

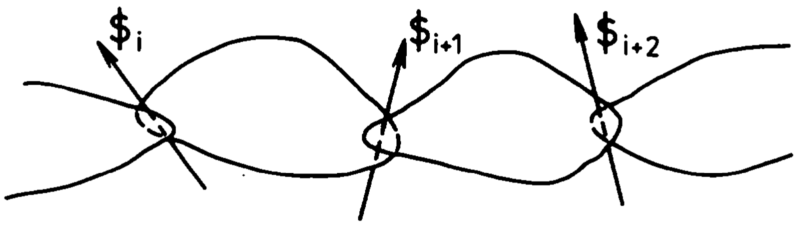

Fig. 2

most common format as a chain. For an open chain of links, the motion of the last relative to the first is determined by superimposing all the individual relative motions. If the joints 1,2,...,N produce motions respectively governed by

$$\underset{\sim}{S}_1 = (\underset{\sim}{\omega}_1, \underset{\sim}{\mu}_1)$$

$$\underset{\sim}{S}_2 = (\underset{\sim}{\omega}_2, \underset{\sim}{\mu}_2)$$

$$\vdots$$

$$\underset{\sim}{S}_N = (\underset{\sim}{\omega}_N, \underset{\sim}{\mu}_N),$$

the resultant relative motion will be given by

$$\underset{\sim}{S} = \sum_{i=1}^{N} \underset{\sim}{S}_i = (\underset{\sim}{\omega}_1+\underset{\sim}{\omega}_2+\ldots+\underset{\sim}{\omega}_N, \underset{\sim}{\mu}_1+\underset{\sim}{\mu}_2+\ldots+\underset{\sim}{\mu}_N).$$

This composite motor is the algebraic representation of what is known as a screw system, and we may write

$$\underset{\sim}{S} = \sum_{i=1}^{N} \omega_i \underset{\sim}{\$}_i,$$

a linear combination of the component ISA vectors. The number of linearly independent component vectors is called the order of the screw system, and cannot exceed six.

The number of apparent relative degrees of freedom of a linkage connection is, in general, equal to the order of its screw system. If the connection is a pure revolute, such as a hinge or a single covalent bond, the screw system of the joint generally has order unity. For a chain of links, even if the total number of apparent relative degrees of freedom between consecutive pairs of links is less than seven, the number will almost certainly, at least for some configurations, be greater than the order of the chain's actual screw system. The term passive degrees of freedom is used in this context.

The screw system of a closed loop is obtained as for an open chain, but with the first and last (1 and N+1) members fastened together rigidly. The screw system of the joints of the closed loop is sometimes called the equivalent screw system (ESS). The linkage will generally have instantaneous mobility of one if, at the instant being considered, the order of the ESS is one less than the total of the apparent relative degrees of freedom of the connections. This total, in the case of a molecular ring, will be the number of single covalent bonds. For full-cycle, or gross, mobility of 1, the order of the ESS must be one less than the same total for almost all possible configurations of the linkage. There is, however, the likelihood of an exceptional configuration, such as a limiting position[4], when the order of the ESS is even lower.

For a screw system of high order, it is sometimes easier to make use of its so-called reciprocal screw system. Two screws, given by

$$\underset{\sim}{\$}_1 = (\hat{\underset{\sim}{\omega}}_1, \hat{\underset{\sim}{\mu}}_1) \qquad \underset{\sim}{\$}_2 = (\hat{\underset{\sim}{\omega}}_2, \hat{\underset{\sim}{\mu}}_2),$$

are said to be reciprocal if and only if

$$\underset{\sim}{\hat{\omega}_1}\cdot\underset{\sim}{\hat{\mu}_2} + \underset{\sim}{\hat{\mu}_1}\cdot\underset{\sim}{\hat{\omega}_2} = 0.$$

Given a screw system, the reciprocal system is that consisting of all the screws which are reciprocal to every screw in the given system. If two systems are reciprocal, the sum of their orders equals six. A linkage of mobility 1 and total number of effective degrees of freedom in its joints equal to N has an ESS of order N-1; the order of its reciprocal screw system is, therefore, 7-N. Thus, a constrained linkage (total number of effective joint freedoms 7) has no reciprocal screws during most of its gross motion. A Bricard linkage (and a flexible cyclohexane molecule) has a single reciprocal screw over most of its cycle, and more at a stationary configuration. A spatial structure with 6 single-degree-of-freedom connections (such as a rigid cyclohexane molecule) may possibly have a configuration which permits instantaneous mobility, of unity, say; in such an event, its screw system is of order 5 and there is a single reciprocal screw for that configuration. We make use of this notion in the worked example below.

The definition of the screw motor has been simplified for the present context, and so the reader must be cautioned against unwarranted inferences. In particular, the definition stated above for $\underset{\sim}{\mu}$ cannot be maintained, in general, once two screws have been combined to produce a third, nor for a screw reciprocal to a given one. In most instances of relative motion, the (non-zero) pitch of the screw must be represented.

SYMMETRIES AND MOBILITY

As mentioned earlier, Dunitz and Waser are able to use a numerical evaluation of freedom and constraint, tempered by various symmetries, to establish mobility or otherwise of certain molecular rings. There are shortcomings in this approach, and the authors are led to the incorrect conclusion that the only significant determinant is a non-intersecting twofold axis of symmetry (known, in the language of spatial linkage kinematics, simply as a line of symmetry).

Symmetries are important, but limited, in their application to the mobility of linkages, and the reader may wish to consult the kinematics literature (Waldron,[12] Baker[13-15]) in this respect. Certainly, the flexible state of the cyclohexane molecule is a result of its line-symmetric form, and line-symmetry will be the determining factor for the existence of conformational isomers of other molecules, such as cycloocta -1,5-diene.

The constitution of a flexible chemical molecule allows it to be identified with a rather simple form of spatial linkage. Specifically, we accept here the properties enunciated in ref. 2 whereby the bond length and bond angle are invariable, although we point out that variations in these parameters could be accommodated, if required, by the methods of linkage kinematics; the relative (torsional) freedoms in the molecule are due to (pseudo-) rotation about each single covalent bond, so that, in the parlance of linkage kinematics, the only joints required are revolutes; because successive single bonds (possibly extended) will always intersect, link-lengths are zero; bond angles may be directly interpreted as angles of skew in the corresponding linkage and (extended) bond lengths as joint offsets. Some of these matters are illustrated in ref. 4.

Having made such an identification, we may immediately conclude that a molecule with 7 or more single covalent bonds is of permanently flexible form, its mobility generally being equal to the quantity by which the number of such bonds exceeds 6. Consequently, obvious cases which can admit of conformational isomers are ones which possess 6 or fewer single covalent bonds. For a linkage to correspond with such molecular conformers, it must be of the octahedral kind; that is, it must be such that its joints can be regarded as edges of a deformable octahedron. Now, Bricard[1] has established that there are precisely 3 distinct types of octahedral linkage. The only one of them which has been effectively utilised in ref. 2 is the line-symmetric case. The plane-symmetric and doubly-collapsible types are potentially just as capable of application to cyclic molecules; it requires only appropriate correspondences between relevant pairs of parameters in order to point to suitable molecules. The matter is not pursued here, because of my lack of knowledge of molecular properties, but, given such a set of properties, it would be a straightforward matter for me to test it for possible mobility of the molecule, by recourse to the characteristics of the 3 types of octahedral linkage.

Mechanical linkages are of practical value because of their gross mobility, and engineering structures because of their rigidity. There is an intermediate state known as instantaneous mobility, which presents something of a functional hazard for a structure, and which is of great significance to other areas of application. It is also the crux of several topics in linkage kinematics. The octahedral linkages which we have discussed above, naturally, manifest full-cycle mobility, and so do the flexible forms of cyclohexane and cycloocta-1,5-diene.

In the latter part of their paper, Dunitz and Waser discuss the apparent paradox of cycloocta-1,4-diene, which they recognise has no non-intersecting twofold axis of symmetry, but for which the Dreiding model appears to be mobile over a short range. The authors conclude that the behaviour of the model can be explained by the proximity of the configuration to one which is line-symmetric. I believe, however, that the authors were victims of the structural basis of their technique. In other words, they were capable of ascribing mobility to no reason other than line-symmetry. In fact, if the model had approximated a mobile line-symmetric configuration, joint tolerances would probably have ensured full-cycle mobility for the device. The reported behaviour exhibited by the model, moreover, is precisely that which characterises practical realisation of instantaneous mechanical mobility and which, in a molecule, I should expect to be duplicated by some kind of vibration in that configuration.

The conformation in question is plane-symmetric; knowledge of the relevant kinematics literature indicates that there is no corresponding linkage, and hence no possibility of full-cycle mobility. In order to explain the evident instantaneous mobility, we call upon the screw system algebra introduced above, and we use our exposition as an example of the applicability of kinematical techniques to conformational analysis.

A WORKED EXAMPLE

We set up an octahedral linkage/cyclic molecular skeleton as shown in Fig. 3, in a boat configuration. It is plane-symmetric, but there is provision for it to represent the cyclohexane ring or one of a range of molecules, such as cycloocta-1,4-diene, as a result of suppressing double bonds, in the manner demonstrated in ref. 2. We are able to put down the following expressions for the elements of the ISA vectors of the 6 joints/single bonds.

$$\hat{\underset{\sim}{\omega}}_1 = \{a_2^2+b_2^2+c_2^2\}^{-\frac{1}{2}}\ (a_2,b_2,c_2)$$

$$\hat{\underset{\sim}{\mu}}_1 = \underset{\sim}{0}$$

$$\hat{\underset{\sim}{\omega}}_2 = \{(a_3-a_2)^2 + (b_3-b_2)^2 + (c_3-c_2)^2\}^{-\frac{1}{2}}\ (a_3-a_2,b_3-b_2,c_3-c_2)$$

$$\hat{\underset{\sim}{\mu}}_2 = \{(a_3-a_2)^2 + (b_3-b_2)^2 + (c_3-c_2)^2\}^{-\frac{1}{2}}\ (b_2c_3-b_3c_2,c_2a_3-c_3a_2,a_2b_3-a_3b_2)$$

$$\hat{\underset{\sim}{\omega}}_3 = \{a_3^2 + (b_4-b_3)^2 + c_3^2\}^{-\frac{1}{2}}\ (-a_3,b_4-b_3,-c_3)$$

$$\hat{\underset{\sim}{\mu}}_3 = \{a_3^2 + (b_4-b_3)^2 + c_3^2\}^{-\frac{1}{2}}\ (-b_4c_3,0,a_3b_4)$$

$$\hat{\underset{\sim}{\omega}}_4 = \{a_3^2 + (b_3-b_4)^2 + c_3^2\}^{-\frac{1}{2}}\ (-a_3,b_3-b_4,\ c_3)$$

$$\hat{\underset{\sim}{\mu}}_4 = \{a_3^2 + (b_3-b_4)^2 + c_3^2\}^{-\frac{1}{2}}\ (b_4c_3,0,a_3b_4)$$

$$\hat{\underset{\sim}{\omega}}_5 = \{(a_3-a_2)^2 + (b_2-b_3)^2 + (c_2-c_3)^2\}^{-\frac{1}{2}}\ (a_3-a_2,b_2-b_3,c_2-c_3)$$

$$\hat{\underset{\sim}{\mu}}_5 = \{(a_3-a_2)^2 + (b_2-b_3)^2 + (c_2-c_3)^2\}^{-\frac{1}{2}}\ (b_3c_2-b_2c_3,c_2a_3-c_3a_2,a_2b_3-a_3b_2)$$

$$\hat{\underset{\sim}{\omega}}_6 = \{a_2^2+b_2^2+c_2^2\}^{-\frac{1}{2}}\ (a_2,-b_2,-c_2)$$

$$\hat{\underset{\sim}{\mu}}_6 = \underset{\sim}{0}$$

For the assemblage to have instantaneous mobility of 1 in the configuration depicted, there must be a single screw which is reciprocal to all 6 of the screws defined above, those 6 ISA vectors belonging to the same 5-system of screws. Let us denote the reciprocal screw by the motor

$$\underset{\sim}{S} = (\alpha,\beta,\gamma,\delta,\varepsilon,\zeta).$$

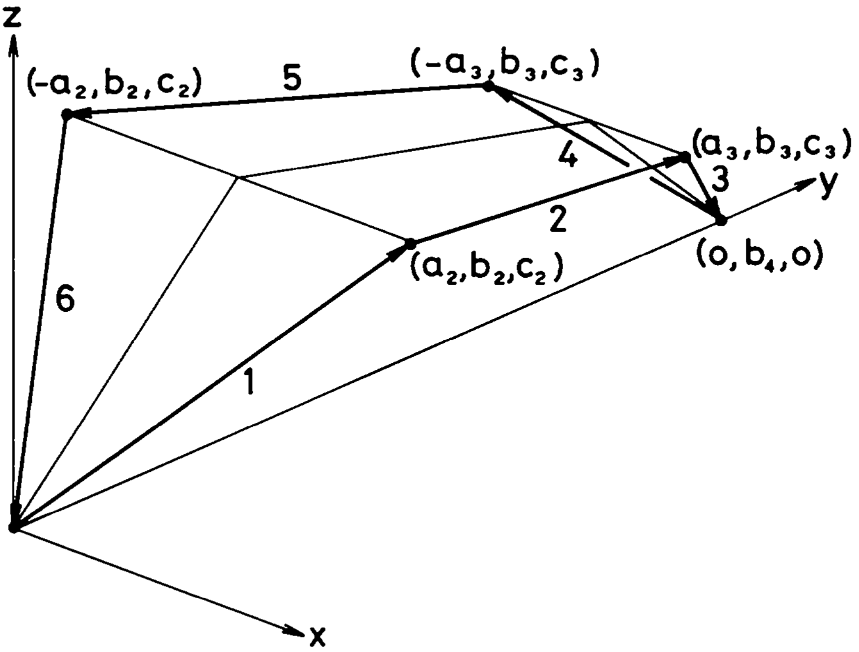

Fig. 3

Then, by the condition stated earlier for reciprocity, taking each of the 6 vectors in turn, we obtain the following equations to be satisfied simultaneously.

$$a_2\delta+b_2\varepsilon+c_2\zeta = 0 \qquad \text{(i)}$$

$$(b_2c_3-b_3c_2)\alpha + (c_2a_3-c_3a_2)\beta + (a_2b_3-a_3b_2)\gamma + (a_3-a_2)\delta + (b_3-b_2)\varepsilon + (c_3-c_2)\zeta = 0 \qquad \text{(ii)}$$

$$-b_4c_3\alpha + a_3b_4\gamma - a_3\delta + (b_4-b_3)\varepsilon-c_3\zeta = 0 \qquad \text{(iii)}$$

$$b_4c_3\alpha + a_3b_4\gamma - a_3\delta + (b_3-b_4)\varepsilon+c_3\zeta = 0 \qquad \text{(iv)}$$

$$(b_3c_2-b_2c_3)\alpha +(c_2a_3-c_3a_2)\beta +(a_2b_3-a_3b_2)\gamma + (a_3-a_2)\delta + (b_2-b_3)\varepsilon +(c_2-c_3)\zeta = 0 \qquad \text{(v)}$$

$$a_2\delta-b_2\varepsilon-c_2\zeta = 0 \qquad \text{(vi)}$$

We deduce at once, from (i), (iii), (iv) and (vi), that

$$\gamma = 0 = \delta$$

$$b_2\varepsilon +c_2\zeta = 0 \qquad \text{(vii)}$$

$$b_4c_3\alpha+(b_3-b_4)\varepsilon+c_3\zeta = 0. \qquad \text{(viii)}$$

From equations (ii) and (v), we see that

either $c_2a_3 = c_3a_2$ (A)

or $\beta = 0$.

In both cases,

$$(b_2c_3-b_3c_2)\alpha+(b_3-b_2)\varepsilon+(c_3-c_2)\zeta = 0. \qquad \text{(ix)}$$

If (A) holds, the result

$$\alpha = \varepsilon = \zeta = 0$$

is acceptable (and, in fact, will be seen to be a consequence). If $\beta = 0$, however, we may conclude from equations (vii)-(ix) that, for a valid solution,

$$\begin{vmatrix} 0 & b_2 & c_2 \\ b_4c_3 & b_3-b_4 & c_3 \\ b_2c_3-b_3c_2 & b_3-b_2 & c_3-c_2 \end{vmatrix} = 0,$$

whence

either $b_2c_3 = b_3c_2$ (B)

or $(b_2-b_4)\, c_3 = (b_3-b_4)c_2$. (C)

Let us consider in turn each of the 3 possibilities for instantaneous mobility.

If (A) holds, axes 1,2,3 and Oy are coplanar, as are 4,5,6 and Oy. That is, axes 2 and 5 either intersect Oy or are parallel to it. Then, the reciprocal screw (which has zero pitch) is coincident with the y-axis, its ISA vector being (0,1,0,0,0,0). Now, the cyclohexane molecule can assume plane-symmetric configurations, such as the chair conformation (in which it is rigid, the configuration being not line-symmetric) and the boat conformation (in which it is flexible, the configuration being also line-symmetric). It is in this latter configuration that condition (A) applies, 4 of the axes intersecting the reciprocal screw and the remaining 2 being parallel to it. The line-geometrical significance of the reciprocal screw in this case and its relationship to the axis of symmetry of the linkage/molecule is discussed in ref. 4.

If (B) applies, we find that

$$\alpha = \frac{1}{c_3}\varepsilon \qquad \zeta = -\frac{b_2}{c_2}\varepsilon ,$$

whence the ISA vector of the reciprocal screw is

$$(1,0,0,0,c_3,-b_3),$$

and its straight-line equation is

$$y = b_3 \qquad z = c_3 .$$

The screw (of zero pitch) is parallel to the x-axis, passing through $(0,b_3,c_3)$. The plane defined by axes 1 and 6, namely

$$z = \frac{c_2}{b_2} y ,$$

contains axes 2 and 5 and the reciprocal screw which, therefore, intersects all 6 axes. The case governed by (C) is the analogous one in which the reciprocal screw (of zero pitch) is parallel to the x-axis and passes through $(0,b_2,c_2)$.

In any of the 3 instances cited, the assemblage of 6 hinges will be instantaneously mobile. Let us now consider the paradox which Dunitz and Waser saw in the flexibility of cycloocta-1, 4-diene in the boat configuration. Portion of the molecule is represented schematically in Fig. 4. By suppressing the double bond CD and extending single bonds BC and ED accordingly, the diagram is directly comparable with Fig. 3.

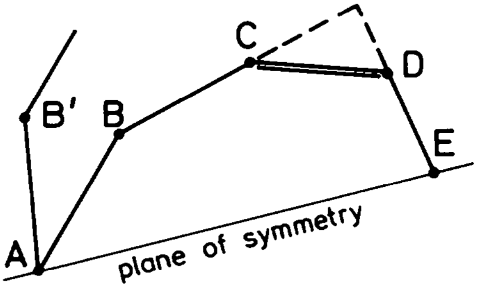

Fig. 4

The most significant fact about this molecule in the present context is that the "torsion" about each of the bonds BC and CD is virtually zero. Consequently, ABCDE is planar, and so axes AB, BC and DE all intersect the line AE, which therefore locates the single reciprocal screw, under condition (A) above. The molecule is thereby mobile in this conformation.

Given values of the various parameters for the ring, it is readily possible to describe the configuration precisely, but little purpose would be achieved here in so doing, particularly since such values are not yet certain. I do mention that, for one set of numbers which I selected from the literature for my own calculations, it was found that bonds AB and DE would be parallel for this configuration of the molecule.

CONCLUDING REMARKS

Considerable space has been devoted in the foregoing to screw system algebra and its application to a specific molecule. The reason for so doing, clearly, was to provide an effective demonstration of the methods at our disposal. It must be again emphasised, however, that kinematical techniques are not restricted to isolated curiosities, but to a wide range of possibilities, a most promising area being that of the analysis of networks of molecules.

REFERENCES

1. R. Bricard, Mémoire sur la théorie de l'octaèdre articulé. *J. math. pures et appl., Liouville* 3, 113-148 (1897).

2. J.D. Dunitz and J. Waser, Geometric constraints in six- and eight-membered rings. *J. Amer. Chem. Soc.* 94, 5645-5650 (1972).

3. O. Bottema, Flexible hexagons. *Proc.K.Ned.Akad.Wet., ser.A* 70, 151-155 (1967).

4. J. Eddie Baker, Limiting positions of a Bricard linkage and their application to the cyclohexane molecule. Submitted to *Mechanism and Machine Theory*.

5. J. Eddie Baker, On linkages and mobile polyhedra. *A.S.M.E. Design Engineering Technical Conf.*, Beverly Hills, Calif., U.S.A., Sep. 28-Oct. 1, 1980. Paper no. 80-DET-30.

6. J. Eddie Baker, On structures and linkages. *Structural Topology* 5, 39-44 (1980).

7. J. Eddie Baker, On mobility and relative freedoms in multiloop linkages and structures. *Mechanism and Machine Theory* 16, 6, 583-597 (1981).

8. T.H. Davies, Kirchhoff's circulation law applied to multi-loop kinematic chains. *Mechanism and Machine Theory* 16, 3, 171-183 (1981).

9. T.H. Davies, Mechanical networks - I. Passivity and redundancy. *Mechanism and Machine Theory* 18, 2, 95-101 (1983).

10. T.H. Davies, Mechanical networks - II. Formulae for the degrees of mobility and redundancy. *Mechanism and Machine Theory* 18, 2, 103-106 (1983).

11. T.H. Davies, Mechanical networks - III. Wrenches on circuit screws. *Mechanism and Machine Theory* 18, 2, 107-112 (1983).

12. K.J. Waldron, Symmetric overconstrained linkages. *J. Engng. Ind., A.S.M.E. Trans., B* 91, 1, 158-164 (1969).

13. J. Eddie Baker, An overconstrained 5-bar with a plane of quasi-symmetry. *Mechanism and Machine Theory* 13, 4, 467-473 (1978).

14. J. Eddie Baker, A compendium of line-symmetric four-bars. *J. Mech. Design, A.S.M.E. Trans.* 101, 3, 509-514 (1979).

15. J. Eddie Baker, On seeking new plane-symmetric six-bars. Submitted to *Mechanism and Machine Theory*.