# Condensed Aromatics.
# Part III. In-Plane Molecular Vibrations of Pyrene

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Z. Naturforsch. **34a**, 876–886 (1979); received April 11, 1979

A new force field is developed for the in-plane vibrations of condensed aromatics using pyrene as a test molecule. Only five parameters are employed in this force field, which improves a four-parameter approximation previously investigated. Still the simple five-parameter approximation gives calculated vibrational frequencies in good agreement with those from the more elaborate Califano-Neto force field.

In the course of the normal coordinate analysis the Hückel molecular orbitals have been deduced. The CC stretching parameters were modified by means of the calculated bond orders. A complete set of independent symmetry coordinates (both in-plane and out-of-plane) for the pyrene molecular model was developed.

New experimental data from infrared and Raman spectra for pyrene are reported.

Also the mean amplitudes of vibration are studied in detail. It is concluded that the simple five-parameter approximation gives reliable mean amplitudes, which undoubtedly are accurate enough for the interpretation of gas electron diffraction data.

Finally the calculated frequencies and mean amplitudes of benzene are given. The mean amplitudes are again found to be very accurate in spite of some substantial inaccuracies in the frequencies.

## Introduction

Conjugated systems in organic chemistry have attracted the interest of many investigators. In the previous parts of this series [1, 2] we have described an extremely simple method of normal coordinate analysis for such systems which gives calculated frequencies in reasonably good agreement with experiment but fails badly when applied to benzene. Since the molecular vibrations of pyrene have been investigated both experimentally [3, 4] and theoretically [4, 5], we have chosen the pyrene molecule (Fig. 1) as a test molecule for a critical review of the simple approximate method [1]. The in-plane and out-of-plane vibrations of this molecule, as well as the other condensed aromatics, are often treated separately. In the present paper we consider only the in-plane force field, but a complete set of symmetry coordinates (both in-plane and out-of-plane) is described.

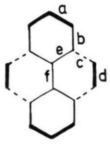

Fig. 1. The different CC bonds in pyrene, drawn with relevance to the calculated bond orders.

The approximation previously developed [1] employs seven parameters of fixed values in the potential function, but a modification of one of these parameters, viz. the CC stretching force constant, is suggested in a prescribed manner. These seven values were used to calculate a multitude of vibrational frequencies, e.g. 48 in naphthalene ($C_{10}H_8$), 72 in pyrene ($C_{16}H_{10}$), 90 in perylene ($C_{20}H_{12}$) and 68 in coronene ($C_{24}H_{12}$). Only four of the parameters pertain to the in-plane vibrations.

On the other hand one has the well known approach of normal coordinate analysis for aromatics due to Califano and Neto with collaborators [5–8], who exclusively treated the in-plane modes. In the following it is referred to as the method of Califano-Neto. In this method 34 in-plane force constants are produced by a subtle theory starting with fewer parameters. It is based on a theory by

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0340-4811 / 79 / 0700-0876 $ 01.00/0

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Scherer et al. [9, 10], which takes into account the Kekulé structures of an aromatic molecule. The force field was successfully applied to different molecules including pyrene [5]. In principle the method of Califano-Neto is simple to use, but when applied to relatively large molecules becomes rather complex in comparison with the simple seven-parameter method.

A part of the purpose of the present work is to see how much is gained by the Califano-Neto method by the increased complexity when compared to the seven-parameter method. In general one can not doubt the superiority of the more complex method for predicting vibrational frequencies. Although the seven-parameter method seems too crude to serve as a reliable aid in making vibrational assignments, it is surprising how well the general picture of the vibrational assignment and a qualitative agreement with observed frequencies is achieved from such a simple method. Another aim of the present work is to produce a modification and possible slight extension of the simple method of approximation in order to improve it without going as fas as Califano-Neto in the complexity. Computed mean amplitudes of vibration [11] are studied in particular in order to investigate the possible usefulness of the simple approximations for this purpose.

Finally we are reporting new experimental Raman and infrared vibrational frequencies for pyrene.

## The Hückel Molecular Orbital (HMO) Model

The molecular orbitals formed from the carbon atomic orbitals in pyrene according to the HMO model [12] fall into the different symmetry species of the $D_{2h}$ group according to

$$\Gamma_\pi = 3\,B_{1g} + 5\,B_{2g} + 3\,A_u + 5\,B_{3u}\,.$$

The $\pi$-energy levels have been obtained and are given in terms of the $x$ values ($x = -2.532$ for the ground state) in Table 1. A representative symmetry-adapted linear combination under each symmetry species is shown in parentheses. For the numbering of the atomic orbitals ($\varphi_i$); see Figure 2.

Table 1. Energy levels in terms of $x$ for the Hückel molecular orbitals of pyrene.

| $B_{1g}$ $(\varphi_1 - \varphi_2 - \varphi_3 + \varphi_4)$ | $A_u$ $(\varphi_1 - \varphi_2 + \varphi_3 - \varphi_4)$ |
|---|---|
| − 1.802 | − 1.247 |
| − 0.445 | 0.445 |
| 1.247 | 1.802 |
| $B_{2g}$ $(\varphi_1 + \varphi_2 - \varphi_3 - \varphi_4)$ | $B_{3u}$ $(\varphi_1 + \varphi_2 + \varphi_3 + \varphi_4)$ |
| − 2.000 | − 2.532 |
| − 0.879 | − 1.347 |
| 1.000 | − 1.000 |
| 1.347 | 0.879 |
| 2.532 | 2.000 |

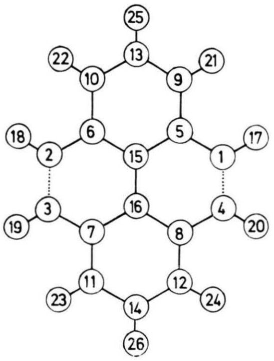

Fig. 2. Numbering of atoms in the pyrene molecular model; symmetry $D_{2h}$. A partial opening of the structure is indicated.

Also the coefficients combining the Hückel molecular orbitals with the sixteen atomic orbitals were all determined. The whole set is too voluminous to be reproduced here. These coefficients were used to calculate the bond orders of the CC distance, $P$, defined in the usual way [12] as numbers between 0 and 1; cf. Table 2.

Table 2. Bond orders, calculated and observed CC bond distances and CC stretching force constants in pyrene.

| Distance type[a] | Calculated bond order | Bond distance [Å] calc. | Bond distance [Å] obs.[b] | Force constant [mdyne/Å] |
|---|---|---|---|---|
| a | 0.669 | 1.397 | 1.380 | 4.871 |
| b | 0.594 | 1.410 | 1.420 | 4.611 |
| c | 0.503 | 1.427 | 1.442 | 4.309 |
| d | 0.777 | 1.379 | 1.320 | 5.257 |
| e | 0.524 | 1.423 | 1.417 | 4.374 |
| f | 0.536 | 1.420 | 1.417 | 4.417 |

[a] See Figure 1. [b] Reference [13].

## Molecular Structure

A planar structure of symmetry $D_{2h}$ was assumed for the pyrene molecule; see Figs. 1 and 2. The structural data were taken from the x-ray work of Camerman et al. [13] with only small modifications to conform exactly with the adopted symmetry. Only $a = 1.382$ Å and $d = 1.325$ Å deviate slightly from the measured bond lengths corrected for rotational oscillations [13] quoted in Table 2. All CH distances were assumed to be 1.08 Å. All bond angles are approximately 120°, none of them deviating more than 2° from this value. Table 2 shows the calculated bond orders ($P$) and CC bond lengths obtained from the $P$ values in the same way as was done for the condensed aromatics previously treated [1]. The agreement with the observed bond distances is satisfactory. A very similar analysis is contained in the crystallographic work [13], where the shortest CC distance (1.320 Å) is discussed in particular.

## Symmetry Coordinates

The normal modes of vibration for pyrene are distributed among the symmetry species of the $D_{2h}$ group according to

$$\Gamma = 13\,A_g + 4\,B_{1g} + 7\,B_{2g} + 12\,B_{3g} + 5\,A_u + 12\,B_{1u} + 12\,B_{2u} + 7\,B_{3u}\,.$$

Some of the species designations vary with different orientations of the cartesian axes. We have chosen $x$ to be perpendicular to the molecular plane while $z$ goes through four atoms and the bond f (see Figure 1).

Figure 2 shows the numbering of atoms and also indicates the "opening" of the structure by neglecting two of the bonds (dotted lines in Figure 2). The "opened" structure has, of course, no physical reality, but is simply a useful aid for identifying redundancies among the coordinates. Let the c type stretchings be identified by $c_1(1\text{–}5)$, $c_2(2\text{–}6)$, $c_3(3\text{–}7)$ and $c_4(4\text{–}8)$. Then the appropriate combinations in the different symmetry species read:

$(A_g)$ $c_1 + c_2 + c_3 + c_4$,
$(B_{3g})$ $c_1 - c_2 + c_3 - c_4$,
$(B_{1u})$ $c_1 + c_2 - c_3 - c_4$,
$(B_{2u})$ $c_1 - c_2 - c_3 + c_4$.

Altogether an independent set of in-plane symmetry coordinates was obtained by taking the appropriate combinations of selected valence coordinates as specified below.

c type CC stretchings (all species),
e type CC stretchings,
f type (middle bond) stretch; $A_g$ species only,
CCC bendings of the type 1–5–15,
CCC 5–15–16 type bendings,
b type CC stretchings,
a type CC stretchings,
CCC 5–9–13 type bendings,
CH 1–17 type stretchings,
CH 9–21 type stretchings,
CH 13–25 type stretchings; only in species $A_g$ and $B_{1u}$,
HCC 5–1–17 type bendings,
HCC 13–9–21 type bendings,
HCC 9–13–25 type bendings; only in species $B_{3g}$ and $B_{2u}$.

Among the out-of-plane coordinates there are two types of linear combinations in the cases where four valence coordinates are symmetrically equivalent. As representative examples we may use (i) the CC torsions $\tau_1(1\text{–}5\text{–}15\text{–}16)$, $\tau_2(2\text{–}6\text{–}15\text{–}16)$, $\tau_3(3\text{–}7\text{–}16\text{–}15)$, $\tau_4(4\text{–}8\text{–}16\text{–}15)$ and (ii) the CH out-of-plane bendings $\gamma_1(5\text{–}4\text{–}1\text{–}17)$, $\gamma_2(3\text{–}6\text{–}2\text{–}18)$, $\gamma_3(7\text{–}2\text{–}3\text{–}19)$, $\gamma_4(1\text{–}8\text{–}4\text{–}20)$. The two types of combinations then read:

i) $(B_{1g})$ $\tau_1 + \tau_2 - \tau_3 - \tau_4$,
$(B_{2g})$ $\tau_1 - \tau_2 - \tau_3 + \tau_4$,
$(A_u)$ $\tau_1 + \tau_2 + \tau_3 + \tau_4$,
$(B_{3u})$ $\tau_1 - \tau_2 + \tau_3 - \tau_4$.
ii) $(B_{1g})$ $\gamma_1 - \gamma_2 - \gamma_3 + \gamma_4$,
$(B_{2g})$ $\gamma_1 + \gamma_2 - \gamma_3 - \gamma_4$,
$(A_u)$ $\gamma_1 - \gamma_2 + \gamma_3 - \gamma_4$,
$(B_{3u})$ $\gamma_1 + \gamma_2 + \gamma_3 + \gamma_4$.

To obtain a complete set of independent symmetry coordinates we have selected the appropriate linear combinations of the following valence coordinates.

CC torsions of the type 1–5–15–16 (all species),
CH out-of-plane bendings of the type 5–4–1–17,
CC out-of-plane bendings of the type 5–6–15–16; only in species $B_{2g}$ and $B_{3u}$,
CC middle bond torsion, type 5–15–16–8; $A_u$ species only,
CC 15–5–9–13 type torsions; only in $B_{2g}$ and $B_{3u}$,
CC 5–9–13–10 type torsions,
CH 13–5–9–21 type out-of-plane bendings,
CH 10–9–13–25 type out-of-plane bendings; only in $B_{2g}$ and $B_{3u}$.

The angle bendings, $\varphi_{ikj}$, were multiplied in the usual way by scaling factors with the dimension of length, viz. $(r_{ik}\, r_{jk})^{1/2}$. Similarly the torsions, $\tau_{ijmn}$, are multiplied by $(r_{ij}\, r_{mn})^{1/2}$, and the out-of-plane bendings, $\gamma_{ijkn}$, by $[(r_{ij}\, r_{jk})^{1/2}\, r_{kn}]^{1/2}$.

## Normal Coordinate Analysis for the In-Plane Vibration

The first column in Table 3 shows the in-plane vibrational frequencies of pyrene calculated by the seven-parameter approximation (4 parameters in the plane). This very simple force field approximation was described and applied to other aromatic molecules previously [1]. The present version uses the refinement of CC stretching force constants obtained in the prescribed way from the reference value of 4.7 mdyne/Å; the resulting values are included in Table 2.

Many modifications of the simple approximation method were tried. In general no substantial improvement of the calculated frequencies was

Table 3. Calculated and observed in-plane frequencies (cm$^{-1}$) of pyrene.

| Species | Simple | | Califano-Neto method | | | Observed | | |
|---|---|---|---|---|---|---|---|---|
| | a | b | [5] | [4] | Present | [3, 14] | [4] | Present[c] |
| $A_g$ | 3039 | 3039 | 3052 | 3081 | 3077 | — | 3102 | 3097 vw |
| | 3031 | 3032 | 3050 | 3073 | 3067 | — | 3059 | 3057 s |
| | 3030 | 3030 | 3046 | 3021 | 3020 | — | 3026 | 3021 vw |
| | 1754 | 1666 | 1570 | 1656 | 1591 | 1630 | 1630 | 1627 vs |
| | 1484 | 1523 | 1516 | 1567 | 1507 | — | 1552 | 1584 s |
| | 1456 | 1475 | 1377 | 1407 | 1384 | 1409 | 1408 | 1405 vs |
| | 1283 | 1294 | 1312 | 1300 | 1298 | 1349 | 1352 | 1359 vw |
| | 1107 | 1148 | 1233 | 1232 | 1237 | 1241 | 1243 | 1236 vs |
| | 1008 | 1051 | 1113 | 1142 | 1119 | 1147 | 1144 | 1142 s |
| | 898 | 919 | 1048 | 1058 | 1047 | 1069 | 1067 | 1066 s |
| | 836 | 834 | 809 | 737 | 804 | — | 805 | 805 w |
| | 490 | 474 | 568 | 607 | 560 | 594 | 593 | 594 s |
| | 377 | 349 | 393 | 393 | 378 | 408 | 408 | 408 s |
| $B_{3g}$ | 3037 | 3038 | 3047 | 3049 | 3047 | — | 3049 ? | 3053 m, sh |
| | 3033 | 3033 | 3045 | 3028 | 3027 | — | 3015 ? | 3011 vw |
| | 1772 | 1655 | 1641 | 1601 | 1611 | 1597 | 1596 | 1642 s |
| | 1533 | 1532 | 1506 | 1509 | 1517 | — | — | 1549 w |
| | 1440 | 1498 | 1382 | 1383 | 1393 | 1372 | 1373 | 1371 m |
| | 1358 | 1422 | 1341 | 1357 | 1353 | — | — | (1359 vw) |
| | 1234 | 1238 | 1205 | 1220 | 1229 | 1201 | — | 1206 vw |
| | 1068 | 1113 | 1157 | 1160 | 1169 | — | 1176 ? | 1174 vw |
| | 1028 | 1058 | 1088 | 1077 | 1075 | 1113 | 1109 | 1107 m |
| | 805 | 774 | 747 | 694 | 751 | — | 736 | 775 vw |
| | 478 | 469 | 481 | 496 | 466 | — | 505 | 505 m |
| | 404 | 415 | 445 | 425 | 431 | — | 458 | 450 m |
| $B_{1u}$ | 3039 | 3040 | 3052 | 3081 | 3077 | 3098 | 3098 | — |
| | 3037 | 3037 | 3046 | 3029 | 3027 | 3080 | 3080 | — |
| | 3030 | 3030 | 3045 | 3020 | 3020 | 3040 | 3040 | 3039 w |
| | 1646 | 1603 | 1571 | 1613 | 1587 | 1528 | 1585 | 1584 w, sh |
| | 1433 | 1482 | 1445 | 1432 | 1462 | 1449 | 1468 | 1462 w |
| | 1358 | 1409 | 1412 | 1418 | 1417 | 1417 | 1449 | 1446 w |
| | 1228 | 1206 | 1242 | 1255 | 1234 | 1242 | 1242 | 1241 m |
| | 1025 | 1040 | 1072 | 1074 | 1067 | 1094 | 1095 | 1095 w |
| | 889 | 908 | 1007 | 982 | 1024 | 1002 | 1064 | 1062 w |
| | 826 | 821 | 835 | 767 | 849 | 820 | 820 ? | 819 w |
| | 653 | 622 | 666 | 651 | 657 | 680 | — | 674 vw |
| | 442 | 448 | 493 | 503 | 485 | 495 | 493 | 496 w |
| $B_{2u}$ | 3033 | 3034 | 3050 | 3073 | 3067 | 3028 | 3028 | 3029 w, sh |
| | 3031 | 3031 | 3047 | 3049 | 3047 | 2989 | 2989 ? | — |
| | 1648 | 1630 | 1577 | 1607 | 1583 | 1597 | 1599 | 1593 w |
| | 1515 | 1576 | 1484 | 1472 | 1490 | 1487 | 1487 ? | 1484 w |
| | 1440 | 1448 | 1425 | 1397 | 1428 | 1432 | 1432 | 1433 m |
| | 1365 | 1441 | 1333 | 1384 | 1348 | 1310 | 1310 | 1312 m |
| | 1160 | 1183 | 1178 | 1172 | 1191 | 1204 | 1272 | 1272 vw |
| | 1044 | 1101 | 1163 | 1169 | 1174 | 1184 | 1204 ? | 1206 m |
| | 1014 | 1035 | 1116 | 1145 | 1124 | — | 1184 | 1185 s |
| | 856 | 870 | 965 | 954 | 973 | 963 | 891 | 963 w/891 w |
| | 630 | 571 | 566 | 506 | 556 | 540 | 537 | 540 w |
| | 315 | 331 | 332 | 355 | 334 | — | 349 | 351 m |

[a] With four parameters [1]. [b] With five parameters (see the text).

[c] Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder.

obtained without adding considerable complexity to the force field. The introduction of a few interaction force constants (one stretch-stretch and one stretch-bend) did not give an appreciable improvement. The final version of our force constant matrix based on internal coordinates (without interaction terms) had the following elements: (i) The CC stretching force constants are maintained as previously (cf. Reference [1] and Table 2). (ii) Also the CH stretching force constants are 5.0 mdyne/Å as before. (iii) $f_\alpha = 0.7$ mdyne/Å (equal to the previous value) is used only for the CCC bendings where an H atom is attached to the central C. (iv) $f_\beta = 0.4$ mdyne/Å is introduced for the three bendings where three CC bonds meet. Hence also outer CCC bendings are included; in pyrene they are of the type 1–5–9; cf. Figure 2. (v) The CCH bending force constants are increased to 0.35 mdyne/Å. The second column of Table 3 shows the calculated frequencies for pyrene with this simple five-parameter in-plane force field. The most significant improvement on comparing with the results of the first column (Table 3) is the lowering of the frequencies around 1750 $\text{cm}^{-1}$ in species $A_g$ and $B_{3g}$.

For the sake of comparison we have also performed a normal coordinate analysis for the in-plane vibrations following the Califano-Neto method [5–8]. We did not hope to reproduce exactly the calculated frequencies of Neto et al. [5] for pyrene because the authors do not report all details of their force field. In contrast to their elaborate treatment of stretching and stretch-stretch interaction force constants they do not seem to take much interest in the bendings. Most of the bend-bend and stretch-bend interactions not mentioned in the cited work [5] we simply set equal to zero. Furthermore we used the transferred rather than adjusted CH stretching force constant. Table 3 shows the very good correspondence between our calculated frequencies according to the method of Califano-Neto and the original ones of Neto et al. [5]. Also included is a set of frequencies computed by Bree et al. [4]. Neither of these authors claim to have reproduced exactly the calculated frequencies of Neto et al. [5], but report to have used a version of the Califano-Neto method.

## Experimental Frequencies

In the course of a systematic experimental study of condensed aromatics we have re-investigated the infrared and Raman spectra of pyrene among many other molecules.

The infrared spectra were recorded on a Perkin Elmer model 225 spectrometer (4000—200 $\text{cm}^{-1}$) and on a Bruker model 114 C fast scan Fourier transform spectrometer (800—40 $\text{cm}^{-1}$). Pyrene was studied as a melt (at approximately 160 °C) and as a polycrystalline film (ambient temperature) between KBr windows. Furthermore, infrared spectra of pyrene as Nujol mull, as pellets in KBr, KI and polyethylene were recorded.

Raman spectra of polycrystalline pyrene were recorded on a modified [15] Cary 81 spectrometer, excited by an argon ion laser (CRL model 52 G) at 90°. The background fluorescence was reduced when pyrene was sublimed *in vacuo* immediately before use.

Table 3 includes a proposed assignment for the fundamentals. The spectra are not discussed in detail since no substantially new features were observed in addition to the previously reported experimental assignments [3, 4, 14].

## Force Constants and Compliants

In our method of computation we start with a diagonal force-constant matrix, say f, in terms of the valence coordinates including all redundancies. In the present case of pyrene it contains the 19 CC stretchings, 10 CH stretchings, 10 CCC bendings of the $\alpha$ type and 18 of the $\beta$ type, and finally the 20 CCH bendings. This matrix contains the five different parameters along its main diagonal. The next step, before solving the vibrational secular equation [11, 16] is to convert f into a symmetrized force-constant matrix F. This step is conveniently executed by means of the T matrix method [17, 18]. A given harmonic force field is not uniquely represented by a matrix f if redundancies are present. A unique representation is, on the other hand, rendered by means of F because the symmetry coordinates (see above) are all independent.

In the five-parameter approximation the typical CC stretching parameters have values around 4.7 mdyne/Å (weighted average for pyrene: 4.61 mdyne/Å). In the Califano-Neto method one starts with CC stretchings from 5.42 to 6.55 mdyne/Å in pyrene (weighted average: 6.13 mdyne/Å). The numerical values of this example may seem to be controversial, but that is not necessarily so. The two force fields need not be drastically different because of this apparent numerical inconsistency. The values should rather be considered as an illustration why one should not speak about CC stretching force constants in aromatic systems at all as if they were independent physical quantities.

If the Califano-Neto force field is expressed in terms of a symmetry F matrix based on the same symmetry coordinates as were used in the f to F transformation, one obtains a sound basis for a comparison of the two force fields. We have also performed this transformation and found a strikingly similar pattern of the two F matrices. For the sake of brevity the complete, large dimension matrices are not reproduced here; the point is sufficiently illustrated by showing only the first block ($A_g$). In Table 4 (five-parameter approximation) and Table 5 (Califano-Neto method) the corresponding matrix elements may be individually compared.

Furthermore, the force constants in Tables 4 and 5 are anomalously large because they compensate for the removal of redundancies when going from f to F. The same phenomenon has been observed in other linked systems, especially of the cage form [17], and is extremely pronounced in the multicage system of a hetero polyanion recently studied [19].

The compliants [11, 20] are known to have physical significance even as isolated quantities unlike the force constants. Consequently one can speak of a compliance for a given CC stretching in a condensed aromatic. Tables 6 and 7 are the $A_g$ blocks of the symmetrical compliance matrices from the two approximation methods. They are simply the inverses of the blocks in Tables 4 and 5, respectively. As expected all the compliants have normal magnitudes. Those of the CC stretchings are around 0.2 Å/mdyne in the case of the five-parameter approximation, and ranging from 0.14 to 0.22 Å/mdyne in the Califano-Neto method. Notice that the CC stretching symmetry coordinates of the $A_g$ species are $S_1$, $S_2$, $S_3$, $S_6$ and $S_7$.

Table 4. The $A_g$ block of the symmetry force-constant matrix in the five-parameter approximation. Units: mdyne/Å.

| No. | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1 | 7.16 | | | | | | |
| 2 | −2.73 | 7.81 | | | | | |
| 3 | −5.48 | 5.23 | 14.95 | | | | |
| 4 | −4.72 | 4.27 | 9.05 | 9.50 | | | |
| 5 | −9.51 | 8.12 | 18.33 | 17.16 | 35.39 | | |
| 6 | 0.00 | −0.02 | 0.01 | 0.00 | 0.05 | 4.62 | |
| 7 | 0.00 | −0.83 | −0.01 | 0.24 | 0.89 | 0.01 | 5.72 |
| 8 | 0.00 | −0.49 | 0.01 | −0.13 | 0.05 | 0.01 | 0.48 |
| 9 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 10 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 11 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 12 | 0.00 | 0.00 | 0.00 | −0.28 | −0.28 | 0.00 | 0.00 |
| 13 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 8 | 1.81 | | | | | | |
| 9 | 0.00 | 5.00 | | | | | |
| 10 | 0.00 | 0.00 | 5.00 | | | | |
| 11 | 0.00 | 0.00 | 0.00 | 5.00 | | | |
| 12 | 0.00 | 0.00 | 0.00 | 0.00 | 0.67 | | |
| 13 | 0.31 | 0.00 | 0.00 | 0.00 | 0.00 | 0.71 | |

Table 5. The $A_g$ block of the symmetry force-constant matrix in the Califano-Neto method. Units: mdyne/Å.

| No. | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1 | 6.94 | | | | | | |
| 2 | −2.48 | 9.96 | | | | | |
| 3 | −5.94 | 7.40 | 19.52 | | | | |
| 4 | −4.79 | 5.35 | 11.57 | 10.97 | | | |
| 5 | −9.82 | 10.31 | 24.06 | 20.39 | 42.52 | | |
| 6 | 0.63 | −0.01 | −0.47 | −0.30 | −0.20 | 6.33 | |
| 7 | −0.35 | −0.20 | 0.12 | 0.46 | 1.38 | 0.61 | 7.70 |
| 8 | 0.09 | −0.44 | 0.00 | −0.11 | −0.03 | 0.07 | 0.38 |
| 9 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 10 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 11 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 12 | 0.28 | −0.14 | −0.28 | −0.52 | −0.77 | 0.00 | 0.00 |
| 13 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | −0.14 | 0.14 |
| 8 | 1.41 | | | | | | |
| 9 | 0.00 | 5.11 | | | | | |
| 10 | 0.00 | 0.00 | 5.05 | | | | |
| 11 | 0.00 | 0.00 | 0.10 | 5.05 | | | |
| 12 | 0.00 | 0.00 | 0.00 | 0.00 | 0.64 | | |
| 13 | 0.29 | 0.00 | 0.00 | 0.00 | 0.00 | 0.67 | |

## Mean Amplitudes of Vibration

The mean amplitudes of vibration, $l$ [11], are important quantities for characterizing non-rigid molecular structures. They are obtainable from the interpretation of gas electron diffraction experiments [21, 22] or, usually more accurately, from spectroscopic computations. A mean amplitude, say $l_{ij}$, is defined for every type of interatomic distance ($i$–$j$), bonded or nonbonded, by the root-mean-square value

$$l_{ij} = \langle (r_{ij} - r_e)^2 \rangle^{1/2} ,$$

where $r_{ij}$ is the instantaneous distance and $r_e$ the equilibrium distance. The mean values should be taken both in the quantum-mechanical and statistical-mechanical sense. Hence the values of $l$ are temperature dependent. In the usual approxi-

Table 6. The $A_g$ block of the symmetry compliance matrix in the five-parameter approximation. Units: Å/mdyne.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| No. 1 | 0.222 | | | | | | |
| 2 | 0.016 | 0.185 | | | | | |
| 3 | 0.018 | −0.029 | 0.193 | | | | |
| 4 | 0.016 | −0.039 | −0.022 | 0.907 | | | |
| 5 | 0.039 | −0.005 | −0.078 | −0.414 | 0.282 | | |
| 6 | −0.000 | 0.001 | 0.001 | 0.004 | −0.003 | 0.217 | |
| 7 | −0.005 | 0.026 | 0.010 | 0.015 | −0.025 | 0.000 | 0.185 |
| 8 | 0.006 | 0.044 | −0.012 | 0.069 | −0.035 | −0.001 | −0.044 |
| 9 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 10 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 11 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 12 | 0.023 | −0.018 | −0.042 | 0.204 | −0.054 | 0.000 | −0.004 |
| 13 | − 0.003 | −0.019 | 0.005 | −0.030 | 0.016 | 0.000 | 0.020 |
| 8 | 0.630 | | | | | | |
| 9 | 0.000 | 0.200 | | | | | |
| 10 | 0.000 | 0.000 | 0.200 | | | | |
| 11 | 0.000 | 0.000 | 0.000 | 0.200 | | | |
| 12 | 0.014 | 0.000 | 0.000 | 0.000 | 1.552 | | |
| 13 | −0.278 | 0.000 | 0.000 | 0.000 | −0.006 | 1.532 | |

mation of small harmonic vibrations [16] the mean amplitudes of planar molecules are independent of the out-of-plane vibrations.

We have computed the mean amplitudes of vibration for pyrene from the three approximate force fields under consideration, viz. those of the simple methods with (a) four, (b) five in-plane parameters, and (c) the Califano-Neto method. All these magnitudes were computed at the temperatures of absolute zero and 298 K. For the sake of brevity only the latter ones are discussed in the following.

### *Bonded Distances*

Table 8 shows the calculated mean amplitudes for the bonded distances. The three methods of approximation are seen to give almost identical results, i.e. the differences are in all but one case about 0.001 Å or less.

### *Nonbonded CC Distances*

The calculated mean amplitudes for all the 31 types of nonbonded CC distances are shown in Table 9. All these types are indicated on Fig. 3 and classified into 10 main groups. Small differences are

Table 7. The $A_g$ block of the symmetry compliance matrix in the Califano-Neto method. Units: Å/mdyne.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| No. 1 | 0.219 | | | | | | |
| 2 | −0.000 | 0.148 | | | | | |
| 3 | 0.015 | −0.039 | 0.184 | | | | |
| 4 | 0.005 | −0.048 | 0.006 | 0.894 | | | |
| 5 | 0.039 | 0.009 | −0.095 | −0.415 | 0.283 | | |
| 6 | −0.020 | −0.006 | 0.009 | 0.026 | −0.019 | 0.164 | |
| 7 | 0.005 | 0.004 | 0.014 | 0.016 | −0.020 | −0.012 | 0.135 |
| 8 | −0.013 | 0.046 | −0.020 | 0.041 | −0.021 | −0.013 | −0.030 |
| 9 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 10 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 11 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 12 | −0.040 | −0.013 | −0.044 | 0.218 | −0.055 | 0.010 | −0.006 |
| 13 | 0.001 | −0.022 | 0.008 | −0.016 | 0.009 | 0.043 | −0.018 |
| 8 | 0.806 | | | | | | |
| 9 | 0.000 | 0.196 | | | | | |
| 10 | 0.000 | 0.000 | 0.198 | | | | |
| 11 | 0.000 | 0.000 | −0.004 | 0.198 | | | |
| 12 | 0.016 | 0.000 | 0.000 | 0.000 | 1.670 | | |
| 13 | −0.348 | 0.000 | 0.000 | 0.000 | −0.003 | 1.664 | |

Table 8. Mean amplitudes of vibration (Å units) for the bonded distances in pyrene at 298 K.

| Distance * | Atom pair ** | a | b | c |
|---|---|---|---|---|
| a | 9–13 | 0.0475 | 0.0475 | 0.0456 |
| b | 5–9 | 0.0477 | 0.0479 | 0.0468 |
| c | 1–5 | 0.0485 | 0.0486 | 0.0477 |
| d | 1–4 | 0.0465 | 0.0465 | 0.0455 |
| e | 5–15 | 0.0474 | 0.0474 | 0.0451 |
| f | 15–16 | 0.0468 | 0.0473 | 0.0469 |
| C–H | 1–17 | 0.0774 | 0.0774 | 0.0772 |
| C–H | 9–21 | 0.0774 | 0.0774 | 0.0772 |
| C–H | 13–25 | 0.0774 | 0.0774 | 0.0772 |

* See Fig. 1. ** For numbering of the atoms; see Fig. 2.

[a] Four-parameter approximation [1].

[b] Five-parameter approximation (see the text).

[c] Califano-Neto method.

Table 9. Mean amplitudes of vibration (Å units) for the nonbonded CC distances in pyrene at 298 K. *

| Type[a] | Atom pair | Distance[b] | a | b | c |
|---|---|---|---|---|---|
| 2a | 1–8 | 2.414 | 0.055 | 0.056 | 0.0538 |
| 2b | 1–15 | 2.460 | 0.055 | 0.057 | 0.0562 |
| 2c | 5–6 | 2.458 | 0.057 | 0.058 | 0.0554 |
| 2d | 5–13 | 2.426 | 0.056 | 0.057 | 0.0546 |
| 2e | 5–16 | 2.452 | 0.055 | 0.057 | 0.0551 |
| 2f | 9–10 | 2.416 | 0.056 | 0.056 | 0.0545 |
| 2g | 9–15 | 2.444 | 0.055 | 0.057 | 0.0540 |
| 2h | 1–9 | 2.506 | 0.066 | 0.064 | 0.0607 |
| 3a | 1–16 | 2.816 | 0.058 | 0.060 | 0.0604 |
| 3b | 5–8 | 2.828 | 0.058 | 0.061 | 0.0591 |
| 3c | 5–10 | 2.820 | 0.060 | 0.061 | 0.0605 |
| 3d | 13–15 | 2.797 | 0.058 | 0.061 | 0.0585 |
| 4a | 1–6 | 3.765 | 0.062 | 0.064 | 0.0610 |
| 4b | 5–7 | 3.747 | 0.061 | 0.062 | 0.0599 |
| 4c | 9–16 | 3.742 | 0.060 | 0.062 | 0.0594 |
| 4d | 1–12 | 3.713 | 0.067 | 0.066 | 0.0630 |
| 4e | 1–13 | 3.760 | 0.068 | 0.067 | 0.0634 |
| 5a | 1–7 | 4.233 | 0.064 | 0.065 | 0.0637 |
| 5b | 1–10 | 4.262 | 0.067 | 0.067 | 0.0652 |
| 5c | 5–12 | 4.247 | 0.065 | 0.067 | 0.0642 |
| 5d | 13–16 | 4.214 | 0.062 | 0.064 | 0.0616 |
| 6a | 1–2 | 4.920 | 0.066 | 0.068 | 0.0662 |
| 6b | 1–14 | 4.840 | 0.068 | 0.068 | 0.0643 |
| 6c | 5–11 | 4.897 | 0.065 | 0.066 | 0.0636 |
| 7a | 1–3 | 5.095 | 0.066 | 0.069 | 0.0676 |
| 7b | 1–11 | 5.067 | 0.067 | 0.068 | 0.0659 |
| 7c | 5–14 | 5.071 | 0.066 | 0.068 | 0.0652 |
| 8 | 9–12 | 5.667 | 0.071 | 0.072 | 0.0690 |
| 9 | 9–11 | 6.161 | 0.069 | 0.071 | 0.0670 |
| 10 | 9–14 | 6.454 | 0.070 | 0.072 | 0.0688 |
| 11 | 13–14 | 7.012 | 0.071 | 0.072 | 0.0692 |

* See also footnotes to Table 8. [a] See Figure 3.

[b] Calculated interatomic distances from the applied structural parameters; Å units.

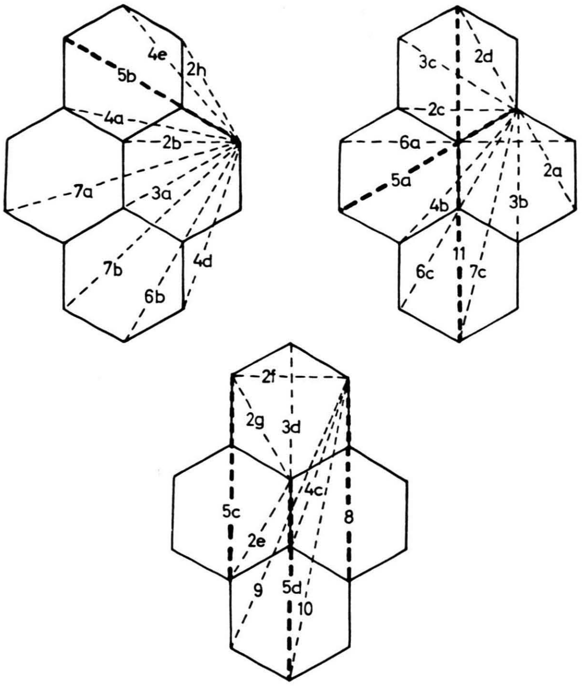

Fig. 3. Classification of the 31 nonbonded CC distances of pyrene. 10 main types are distinguished.

noted between the results from approximations (a) and (b), but here we are most interested in the comparison between the five-parameter approximation (b) and the Califano-Neto method (c). The latter set (c) is supposed to contain the most accurate values. The agreement is seen to be good since 26 out of the 31 amplitudes have differences less than 0.003 Å, and the largest are about 0.004 Å.

### *Nonbonded CH Distances*

Table 10 shows the calculated mean amplitudes for the 39 types of nonbonded CH distances. Only the results from the five-parameter approximation (b) and the Califano-Neto method (c) are included. The 39 CH distances have been collected into 15 main groups; see Figure 4. Very good agreement is found for the results from the two approximations: in 21 out of the 39 cases the differences are 0.001 Å or less, in 15 cases 0.002 Å or less, while the largest discrepancies (3 cases) are about 0.003 Å.

### *The HH Distances (Nonbonded)*

Calculated mean amplitudes for the 15 types of HH distances are shown in Table 11. For the sake of brevity only the results from the Califano-Neto

Table 10. Mean amplitudes of vibration (Å units) for the nonbonded CH distances in pyrene at 298 K.*

| Type[a] | Atom pair | Distance | b | c |
|---|---|---|---|---|
| 2A | 1–20 | 2.079 | 0.100 | 0.099 |
| 2B | 5–17 | 2.184 | 0.101 | 0.101 |
| 2C | 5–21 | 2.172 | 0.101 | 0.100 |
| 2D | 9–25 | 2.128 | 0.101 | 0.099 |
| 2E | 13–21 | 2.138 | 0.100 | 0.099 |
| 3A | 1–21 | 2.745 | 0.130 | 0.129 |
| 3B | 9–17 | 2.741 | 0.131 | 0.130 |
| 4A | 5–20 | 3.392 | 0.097 | 0.096 |
| 4B | 5–25 | 3.402 | 0.097 | 0.096 |
| 4C | 9–22 | 3.388 | 0.097 | 0.096 |
| 4D | 15–17 | 3.436 | 0.098 | 0.097 |
| 4E | 15–21 | 3.426 | 0.097 | 0.095 |
| 5A | 5–22 | 3.900 | 0.095 | 0.094 |
| 5B | 15–19 | 3.896 | 0.094 | 0.094 |
| 5C | 15–25 | 3.877 | 0.095 | 0.093 |
| 6A | 1–24 | 4.063 | 0.131 | 0.130 |
| 6B | 13–17 | 4.115 | 0.132 | 0.130 |
| 7A | 1–25 | 4.631 | 0.111 | 0.108 |
| 7B | 5–18 | 4.636 | 0.108 | 0.106 |
| 7C | 9–20 | 4.584 | 0.110 | 0.108 |
| 7D | 15–23 | 4.619 | 0.107 | 0.106 |
| 8A | 5–24 | 4.886 | 0.121 | 0.120 |
| 8B | 9–18 | 4.894 | 0.122 | 0.121 |
| 9A | 1–22 | 5.342 | 0.099 | 0.097 |
| 9B | 5–19 | 5.313 | 0.097 | 0.096 |
| 9C | 15–26 | 5.294 | 0.097 | 0.095 |
| 10A | 1–18 | 5.885 | 0.106 | 0.105 |
| 10B | 1–26 | 5.796 | 0.107 | 0.105 |
| 10C | 5–23 | 5.863 | 0.105 | 0.104 |
| 10D | 13–19 | 5.799 | 0.107 | 0.105 |
| 11A | 1–19 | 6.148 | 0.102 | 0.101 |
| 11B | 1–23 | 6.125 | 0.101 | 0.099 |
| 11C | 5–26 | 6.124 | 0.101 | 0.099 |
| 11D | 9–19 | 6.119 | 0.101 | 0.100 |
| 12 | 9–24 | 6.290 | 0.127 | 0.125 |
| 13 | 9–23 | 7.063 | 0.112 | 0.110 |
| 14 | 13–23 | 7.217 | 0.121 | 0.119 |
| 15 | 9–26 | 7.517 | 0.104 | 0.101 |
| 16 | 13–26 | 8.092 | 0.103 | 0.100 |

* See also footnotes to Tables 8 and 9. [a] See Figure 4.

method are given. On comparing with the results from the five-parameter approximation again a very good agreement was found: most of the differences are below 0.002 Å, the largest one being about 0.003 Å.

### *Conclusion*

In conclusion it is found that the simple approximate methods, and in particular the five-parameter approximation developed in the present work, give very good calculated mean amplitudes of vibration, within about 0.004 Å (in most cases appreciably less) when compared to the more elaborate Califano-Neto method. The approximate mean amplitudes obtained in this way are undoubtedly accurate enough to be useful in the interpretations of modern gas electron diffraction measurements.

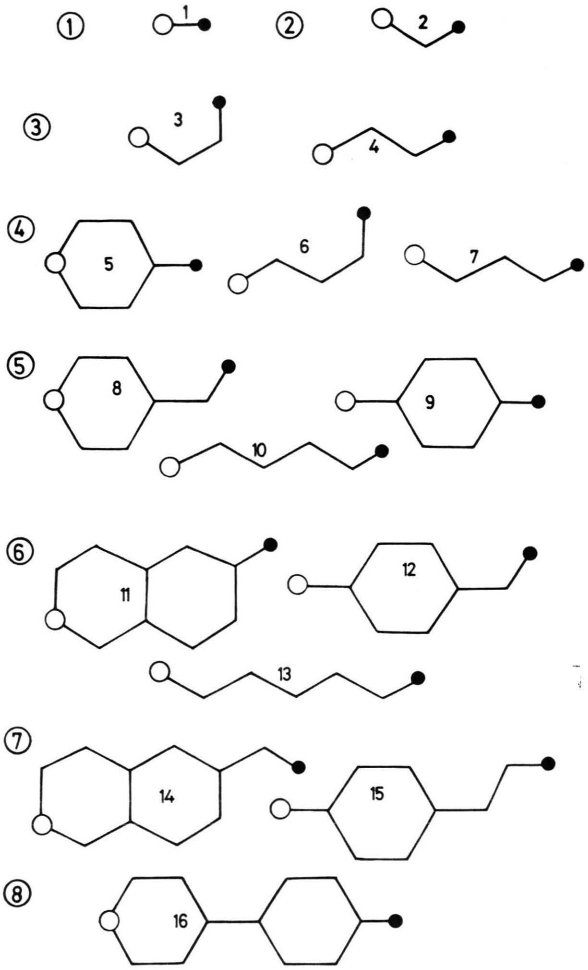

Fig. 4. Survey of the 16 main types of CH distances (1 bonded and 15 nonbonded), which occur in pyrene. Encircled numbers indicate the number of bonds which separate the C and H atoms in question.

## Benzene

In the first paper of this series [1] the failure of the simple approximation with four in-plane parameters was pointed out when applied to benzene. When the five-parameter approximation

Table 11. Mean amplitudes of vibration (Å units) for the HH distances in pyrene at 298 K according to the Califano-Neto method. *

| Atom pair | Distance | Mean amplitude |
|---|---|---|
| 17–20 | 2.382 | 0.159 |
| 21–25 | 2.448 | 0.158 |
| 17–21 | 2.536 | 0.184 |
| 21–22 | 4.270 | 0.132 |
| 17–24 | 4.751 | 0.167 |
| 17–25 | 4.806 | 0.167 |
| 17–22 | 5.956 | 0.143 |
| 17–26 | 6.704 | 0.138 |
| 21–24 | 6.776 | 0.171 |
| 17–18 | 6.803 | 0.137 |
| 17–23 | 7.185 | 0.124 |
| 17–19 | 7.208 | 0.125 |
| 21–23 | 8.009 | 0.136 |
| 21–26 | 8.255 | 0.143 |
| 25–26 | 9.172 | 0.124 |

* See footnotes to Tables 8 and 9.

is employed to benzene an over-all improvement of the calculated frequencies is achieved. Table 12 shows the calculated frequencies according to this approximation along with the results from the Califano-Neto method. The latter set stems from our recalculation, which agrees satisfactorily with the original data of Neto et al. [7]. Nevertheless there are still some serious discrepancies in the frequencies obtained by the two methods, the largest one occurring for the lowest $A_{1g}$ frequency.

Table 12. Calculated in-plane frequencies (cm$^{-1}$) for benzene

| Species | Methods | |
|---|---|---|
| | Simple [a] | Califano-Neto |
| $A_{1g}$ | 3030 | 3063 |
| | 794 | 993 |
| $A_{2g}$ | 1386 | 1361 |
| $E_{2g}$ | 3037 | 3046 |
| | 1614 | 1607 |
| | 1104 | 1166 |
| | 652 | 605 |
| $B_{1u}$ | 3042 | 3044 |
| | 1136 | 1021 |
| $B_{2u}$ | 1551 | 1314 |
| | 1141 | 1174 |
| $E_{1u}$ | 3031 | 3055 |
| | 1483 | 1480 |
| | 910 | 1025 |

[a] Five-parameter approximation; only four of the parameters are relevant for benzene.

Table 13. Mean amplitudes of vibration (Å units) for benzene at 298 K.

| Type | Distance [a] | Simple [b] | Califano-Neto | Rigorous [11] |
|---|---|---|---|---|
| Bonded | | | | |
| C—C | 1.397 | 0.0475 | 0.0458 | 0.04635 |
| C—H | 1.084 | 0.0774 | 0.0772 | 0.07705 |
| Nonbonded | | | | |
| C ··· C | 2.420 | 0.0562 | 0.0549 | 0.05517 |
| C ··· C | 2.794 | 0.0599 | 0.0610 | 0.05899 |
| C ··· H | 2.154 | 0.1004 | 0.0992 | 0.09984 |
| C ··· H | 3.402 | 0.0970 | 0.0959 | 0.09689 |
| C ··· H | 3.878 | 0.0941 | 0.0947 | 0.09337 |
| H ··· H | 2.481 | 0.1586 | 0.1575 | 0.15798 |
| H ··· H | 4.297 | 0.1330 | 0.1314 | 0.13316 |
| H ··· H | 4.962 | 0.1189 | 0.1192 | 0.11817 |

[a] Calculated interatomic distances in Å.
[b] Five-parameter approximation.

In spite of the substantial inaccuracies in the calculated frequencies it may be concluded that the mean amplitudes of vibration from the five-parameter approximation are very good for benzene. On comparing with the results from the Califano-Neto method all differences at 298 K are found to be less than 0.002 Å (see Table 13). A set of mean amplitudes for benzene from a rigorous calculation [11] are included in Table 13. These values were obtained on adjusting the force field accurately to a set of experimental frequencies. The rigorous values are seen to be in good agreement with both sets of the present calculations; it can actually not be concluded with certainty which one of the two present methods is best. It does appear, however, that the simple five-parameter approximation is as good as the Califano-Neto method for the purpose of computing the mean amplitudes of vibration.

### *Acknowledgement*

Financial support to BNC from the Norwegian Research Coucil for Science and the Humanities is gratefully acknowledged.

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